Interactive comment on "An apportionment method for the Oxydative Potential to the atmospheric PM sources: application to a one-year study in Chamonix, France" by Samuël Weber et al.

This paper uses a PMF analysis to determine the sources of PM10 OP measured with two assays, ascorbic acid (AA) and dithiothreitol (DTT). A multiple regression analysis is then used to derive a linear model to predict the OP for each assay with sources as the independent variable. This model provides the intrinsic OP (OP/mass) for each source. Relative contributions of the sources to PM10 mass and the OP for each assay are contrasted. The results are interesting and add more general insight into these assays. However, there are a number of issues. 1) The PMF/multiple regression analysis approach on OP has been done before (Bates et al). This should be recognized and more comparisons between this and the Bates method provided. This is not a novel idea, as seems to be indicated in the Abstract. 2) After noting that a current issue with various studies investigating OP of aerosols is the lack of a standard method, the authors utilize a non-standard method for the OP assay. This makes comparisons with other reported studies difficult. 3) The authors use PM10 in the analysis, which leads to further difficulties in comparing with other studies (many are PM2.5) and makes the source apportionment much more complicated. Furthermore, it raises the possibility of greater artifacts arising in the OP analysis due to interactions between aerosol chemical species that are not mixed in the ambient aerosol, or likely to be mixed when deposited in the respiratory system. Although this adds to the confusion when comparting OP results, the results are of sufficient interest for publication in this journal. Specific comments follow.
Authors thank this referee for his useful review. We tried out to answer him in the following discussion.

Pg 2 Line 1. Specifically explain how OP measurements relies on surface area and particle size
The OP is a measure of reactivity between some antioxidants or surrogates (AA or DTT) and the PM. The reactivity is function of the chemistry and the number of reaction site. The particle size depends on several factors, along them the chemistry and the lifetime PM (Gehling and Dellinger, 2013). Furthermore, the higher the surface area is, the more likely the number of reaction site is. Surface area and particle size regarding OP measurements was also addressed specifically by (Sauvain et al., 2013). These references were added in the manuscript.

Gehling, W., & Dellinger, B. (2013). Environmentally persistent free radicals and their lifetimes in PM2. 5. Environmental science & technology, 47(15), 8172-8178.
Sauvain, J.-J., Rossi, M.J., Riediker, M., 2013. Comparison of three acellular tests for assessing the oxidation potential of nanomaterials. Aerosol Science and Technology 47, 218-227.

Pg 2 lines 17 to 25: Issues with PMF. This paragraph is rather opaque and possibly unnecessary. First, PMF analysis of aerosol data sets is now very common practice, so many of the issues have been addressed. Thus it is not clear why such detailed discussions are included. It would be better to refer to some of the original papers. Furthermore, a number of investigators have reported using PMF on OP data. These should also be cited. A better literature review by the authors is warranted.
In this paragraph we explain why we didn't estimate the OP with the chemical species as explanatory variable but with the PMF sources instead. We explain what are the possible biases if we assess the

linear regression directly with the chemical species and how using sources' contribution instead mitigate them.
We modified the text as follows:

Another option is to consider the sources contribution instead of the chemical species (Bates et al., 2015; Fang et al., 2015, 2016; Verma et al., 2014). Indeed, working directly with chemical species involves assessing an exhaustive composition characterization. This is rather impossible since many species in the complex mixture of aerosols remain unidentified. Moreover, if a detailed composition (which can sometimes include up to 150 species (Waked et al., 2014)) is provided, at least the same number of samples for OP measurements is needed, otherwise, the system remains underdetermined. Reducing the system by direct truncation is not possible since species contributing to OP could be dropped, inducing some degree of unknown bias. Conversely, if the explanatory variables are the sources' contributions, biases are mitigated.
However, the sources dynamics need to be determined for a long period of time in order to reflect the climatology of the location. Moreover, the composition of a given named source may vary according to its location (Belis et al., 2013).
To mitigate these issues, we decide to use a PMF approach instead of a CMB model to better render the local specificities of the sources. Indeed, the CMB averages the sources profil's from different studies and is then locally biased. Furthermore, in this study a whole year of analysis is used as input of the PMF. We then have a climatological view of the sources dynamics.

Bates, J. T., Weber, R. J., Abrams, J., Verma, V., Fang, T., Klein, M., Strickland, M. J., Sarnat, S. E., Chang, H. H., Mulholland, J. A., Tolbert, P. E. and Russell, A. G.: Reactive oxygen species generation linked to sources of atmospheric particulate matter and cardiorespiratory effects, Environ. Sci. Technol., 49(22), 13605–13612, doi:10.1021/acs.est.5b02967, 2015.

Belis, C. A., Karagulian, F., Larsen, B. R. and Hopke, P. K.: Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe, Atmos. Environ., 69, 94–108, doi:10.1016/j.atmosenv.2012.11.009, 2013.

Fang, T., Guo, H., Verma, V., Peltier, R. E. and Weber, R. J.: PM2.5 water-soluble elements in the southeastern United States: automated analytical method development, spatiotemporal distributions, source apportionment, and implications for heath studies, Atmospheric Chem. Phys., 15(20), 11667–11682, doi:10.5194/acp-15-11667-2015, 2015.

Fang, T., Verma, V., Bates, J. T., Abrams, J., Klein, M., Strickland, M. J., Sarnat, S. E., Chang, H. H., Mulholland, J. A., Tolbert, P. E., Russell, A. G. and Weber, R. J.: Oxidative potential of ambient water-soluble PM 2.5 in the southeastern United States: contrasts in sources and health associations between ascorbic acid (AA) and dithiothreitol (DTT) assays, Atmospheric Chem. Phys., 16(6), 3865–3879, doi:10.5194/acp-16-3865-2016, 2016.

Verma, V., Fang, T., Guo, H., King, L., Bates, J. T., Peltier, R. E., Edgerton, E., Russell, A. G. and Weber, R. J.: Reactive oxygen species associated with water-soluble PM2 in the southeastern United States: spatiotemporal trends and source apportionment., Atmospheric Chem. Phys., 14(23), 12915–12930, doi:10.5194/acp-14-12915-2014, 2014.

Pg 4 lines 19 to 21. Explain specifically how meteorology and inversions increase correlations between measured species. Take inversions, for example, how is co-variability affected by a factor that changes concentrations of all independent variables by roughly the same amount?

We add in the manuscript the following explanation:

"During temperature inversion in Alpine valley, pollutants are stuck into the Atmospheric Boundary Layer (ABL) and cannot be removed by wind. Such inversion may be stable during several days. As a result, the different emission sources during that period of time add together and the dynamic from the different sources is masked. In other word, one sample does not integrate anymore only emissions during the sampling time, but also emissions of the previous days. This end-up with chemical species in one sample that should not be present together, respect to the temporality of their respective sources. Thereby, their correlation is increased".

Pg 4 line 32, what does geochemically sounded mean?
We didn't want to constraint to much the PMF. We then decided to put a minimal amount of constraint based on our prior knowledge of the sources.
We modified our sentence as follows:

A minimal set of constraints based on prior and external geochemical knowledge of sources fingerprints was applied

Pg 5, what does pulled up maximally mean?
"Pull up" refer to an option of the EPA PMF5.0 software:
- Pull up try to increase the amount of the desired specie in the given factor
- Pull down does the opposite.

Shortly, the new solution of the PMF differs from the previous one from a certain amount dQ, and the PMF software let use choose the strength of the variation (Pull up / pull up maximally). For further details, refer to the EPA PMF5.0 userguide.
We modify the following explanation in the text:

- *in the biomass burning factor, the contributions of levoglucosan, potassium, methoxyphenols and Bcbb were increased, whereas the Bcff and HOP were set to 0,*
- *HOP was increased in the vehicular factor.*

We increased the concentration of the species in the factors thanks to the "pull up maximally" option of the EPA PMF5.0 software (US EPA, 2017), which try to increase the contribution of the given specie to the factor.

Was the DTT assay performed in simulated lung fluid (SLF)? If so, this deviates from the standard DTT protocol as described by Cho et al, 2005. This means the DTT activities reported in this work cannot necessarily be compared to most other published work, which follow the Cho method. This issue is important since it potentially adds confusion to the public literature on OP. This should be made very clear in the Abstract, Conclusions etc. Optimally, a conversion factor comparing this SLF_DTT to the standard method DTT activities would be included in the paper to help in interpreting the results. It is rather surprising these authors have done this given statements in the paper on limitations with no standard method used in practice (ie, the statement is made, then a non-standard practice is utilized).

DTT assay was performed after a PM extraction in SLF according to Calas et al., 2017. As shown by Calas et al., 2017 OP results after SLF extraction diverge by a little % with regards to a water extraction as done by Cho et al., 2005. Our protocol post-extraction is performed according to Charrier

et al., 2012 which have modified Cho et al., 2005, carried out Chelex-treated phosphate buffer to remove trace metal contamination. In fact, Cho et al., (according to Kumagai et al., 2022) used EDTA to purify the phosphate buffer leading to further metal effect inhibition during the assay. Finally, the percentage or conversion factor is not predictable between OP(SLF_DTT) and OP DTT since the extraction in SLF is mimicking the contact between particles and lung epithelium and some components might be complexed or not as in physiologic conditions.
We clarified the use of this protocol in the abstract and possible limitations of the study

We add the following limitation:

First of all, when comparing with others previous studies we should note that our PM extraction of samples were done in a SLF and not in water. This induces a difference of several percent in OP measurement which is not predictable for the complexes occurring between PM and SLF compounds as when PM enters in contact with the epithelial lung fluid (Calas et al., 2017), and then direct comparison may not be fully accurate.

Pg 5 Section 2.4 Does the filter extraction method include only water soluble species or both water and water insoluble species. For example, does the method extract BC? It is later stated that BC is correlated with the measured OP, but it is unclear if the assays are actually exposed to BC. More details on the extraction method are needed.

We agree with the reviewer and added this sentence to clarify our protocol:

The filter extraction method includes both water soluble and insoluble species. After the SLF extraction, particles removed from filter are not filtrated; the whole extract is injected in the multiwall plate.

No discussion given on blanks, which are critical in OP measurements. Is the OP data blank corrected?
Three filter blanks are included in every plate (OP AA and OP DTT) of the protocol. The value of the blank are then deduced from the sample measurement.
This was added in the methodology section:

Three filter blanks are included in every plate (OP AA and OP DTT) of the protocol. The value of the blank are then deduced from the sample measurement.

Pg 5 line 26, the unit nmol min-1 m-1 is incorrect.
Modified accordingly nmol min^{-1}m^{-3}. Thanks for your attentive review.

Pg 6 line 19, typo, has shows. . .
Thanks. Corrected to "shows".

Pg 6 line 20 and 21. What does the following line mean? . . . This underlines that the assays are sensitive to different ROS. . .. Is it being asserted that the assays are measuring ROS on the particle? This is not what these assays are designed to measure. I think the line gives a false impression, versus what the authors really mean.
We apologize for the misunderstanding, DTT and AA assays are indirect ROS measurements.
We corrected our sentence as follows:

This underlines that the assays are sensitive to different chemicals species carried out by PM.

Fig 10. The vehicular source does not appear constant throughout the year. The mean is very likely higher during cold seasons versus warm seasons, contrary to what is stated in the paper Any explanation?
In Alpine valley some strong and persistent inversion layer occurs during winter. This leads to accumulation of pollutant in the ABL. As a result, even if the emission is constant, the concentration of the vehicular source increases during winter.
We modify the text as follows:

The vehicular source is quite constant all over the year. Indeed, the higher concentration during winter may be attributed to accumulation in the ABL, and not to an increase of emission.

How is the multiple regression analysis performed in this paper novel relative to the published results of Bates et al (which is cited)? A detailed contrast would be valuable since it appears this paper is following, in general, the same approach as Bates et al. Or maybe it differs?
Indeed, we use a quite similar approach as there is not so many way to perform a multiple linear regression. However, there are several points where we differ.
First of all, in the backward elimination, Bates et al decided to base their rejection criteria on the p-value. We decided to remove a source based on its negativity. Indeed, we may have a statistically significant negative value. But according to us, a source with negative intrinsic OP does not have a geo-chemical sens as the air is known to be a strong oxidant milieu.
Secondly, the approach of Bates et al, uses ordinary least square (OLS). However, as we have an estimation of our measurements uncertainty, we use a weighted least square (WLS) regression.
Finally, we propose a way to estimate the uncertainty of our estimated OP thanks to a Monte-Carlo method, which is not provided in the previous study.
Moreover, the method proposed here does not only include the multiple linear regression (MLR) but also the use of the PMF model instead of the CMB one. Indeed, the MLR is highly sensitive to the explanatory variable and we decide to use the local sources' profile (PMF) instead of the chemical mass balance method with ensemble-averaged source impact profiles.

We add the following paragraph to explain the differences between the two methods:

The method proposed here is an improvement of the one of Bates et al (2015) and our methods differ in several points.
First of all, our backward elimination criteria is based on the negativity of a source and not in its p-value. Indeed, a source might present a statistically significant negative value. But according to us, a source with negative intrinsic OP does not have a geo-chemical sense as the air is known to be a strong oxidant milieu.
Secondly, as Bates et al (2015) didn't measure the uncertainty of their OP samples, they used an ordinary least square (OLS) regression. On the opposite, we have an estimation of our measurements uncertainty thanks to triplicate. We then use a weighted least square (WLS) regression instead.
Finally, we propose a way to estimate uncertainties of our estimated OP with a Monte-Carlo method, which is not provided in the previous study.
Moreover, the method proposed here does not only include the multiple linear regression (MLR) but also the use of the PMF model instead of the CMB one. Indeed, the MLR is highly sensitive to the explanatory variable and we decide to use the local sources' profile (PMF) instead of the chemical mass balance method with ensemble-averaged source impact profiles.

Pg 8, line 35. Why does the OP never display negative values? Is it because they were thrown out in the data set, ie samples with low masses where not included. These would be cases where the measurements would be near the detection limits and negative values possible. This needs more explanation as it can bias the results.

Some samples were not analyzed due to the too low PM mass impacted in the filters. In all analyzed samples, the OP (AA and DTT) never displays negative value. This is also true for the samples with the lowest PM mass. Indeed, days with low mass are not necessary day with low OP or near detection limit. We discarded these days only to have comparable data, based on the same protocol for the extraction and measurement (since DTT assay can display non-linear response when you are not extracting at iso-mass concentration (Charrier et al., 2016)) .

As a result, we don't think that the exclusion of days with too low mass induces a bias in the OP and could hide the possible negative OP for these days. As far as we know, the OP of these days may be high, low or negative. But of course, as we did not measure these sample, this is only an assumption.

Pg 9, line 1. A non-zero intercept is also possible due to sampling artifacts associated with the filter sampling. Un-denuded sampling onto quartz filters are known to have positive artifacts. Add a discussion on possible effects of filter artifacts on this analysis.

We are not sure to fully understand the reviewer as the question seems to mix chemistry-related and OP-related issues. However, we definitively agree that impacts of the sampling artifacts is a very important topic, most probably for both aspects.

Sampling artifacts of PM with filters is well known. However, to the best of our knowledge, no previous study focused on the specific point of how it impacts PMF studies. This is indeed an intricated issue since PMF requires chemical profiles of sources which are rather stable in time, while sampling artifacts are by nature dependent upon the pressure and temperature of sampling. We may point out that Favez et al. (2010) (among other studies) did source apportionment inter-comparison between off-line samples (filters) and AMS sampling, and found a relatively good agreement between the different techniques that are not prone to sampling artifacts in the same way. Therefore, the impact of artifact may be mitigated for source apportionment.

When it comes to the impact of sampling artifacts on OP measurements, it also has been shown recently that heterogeneous reactions may happen between the gaseous oxidant (ozone, free radical) and the surface of the filter (Malynuk et al., 2015). Such reaction may have an impact on the OP measurements from filter sampling. However, again, there is no specific work presented in the literature on the direct impact of the change in chemistry linked to sampling artefact on the OP measurements.

Nevertheless, the paragraph of our article quoted for this remark do not refer to this topics. We compared OP measured and OP modeled and compute the linear regression between them. Therefore, we work on the "on-filter OP", and it does not seem a point to discuss sampling artifact in this context. But we fully agree with the reviewer that OP measured on the filter may not reflect actual OP in the real atmosphere. Some in depth study related to OP of semi-volatile species are needed to estimate the "sampling artifact of OP". Again, to the best of our knowledge, no study was focused in this specific issue yet, and our data do not allow such investigations.

Melymuk, L., Bohlin-Nizzetto, P., Prokeš, R., Kukučka, P. and Klánová, J.: Sampling artifacts in active air sampling of semivolatile organic contaminants: Comparing theoretical and measured artifacts and

evaluating implications for monitoring networks, Environmental Pollution, 217, 97 106, doi:10.1016/j.envpol.2015.12.015, 2016.

Favez, O., El Haddad, I., Piot, C., Boréave, A., Abidi, E., Marchand, N., Jaffrezo, J.-L., Besombes, J.-L., Personnaz, M.-B., Sciare, J., Wortham, H., George, C. and D Anna, B.: Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France), Atmospheric Chemistry and Physics, 10(12), 5295 5314, doi:10.5194/acp-10-5295-2010, 2010.

Pg 10 line 13 and 14. These assays do not measure the ability to generate ROS, they measure the depletion of the antioxidant. There is a big difference.
We apologize for the confusion and perfectly agree. This is a big shortcut that does not take into account the numerous chemical reactions that might occur.
We rephrase the following sentence:
The various sources do not have the same ability to generate ROS.

By:
The various sources do not have the same reactivity toward the AA and DTT.

Pg 10 Regarding the discussion comparing the intrinsic OP levels. Why not compare to other reported intrinsic values? For DTT, see for example, Shiraiwa et al (Shiraiwa, M., K. Ueda, A. Pozzer, G. Lammel, C. J. Kampf, A. Fushimi, S. Enami, A. M. Arangio, J. Frohlich-Nowoisky, Y. Fujitani, A. Furuyama, P. S. J. Lakey, J. Lelieveld, K. Lucas, Y. Morino, U. Poschl, S. Takahama, A. Takami, H. Tong, B. Weber, A. Yoshino, and K. Sato (2017), Aerosol health effects from molecular to global scales, Envir. Sci Technol. , 51, 13545-13567). Keep in mind that much data is likely PM2.5.
Pg 10. When comparing the results of this study to others, eg, Bates, et al., Fang et al., Verma et al., Charrier et al., keep in mind that those studies were PM2.5 not PM10, which could have a significant effect. Furthermore, the assay was performed differently in this study.

This study is intended to be focused on the methodology and provides only a study case. We didn't aimed at going into too much interpretation of the Chamonix results. However, a incoming study with other sites will compare our results to previous studies in much more details.
Also, as you pointed out, our study is on PM10 and with a singular extraction protocol. We then should be very cautious when comparing the intrinsic OP levels with other study as it was already reported that the OP may vary or not within the size of the PM (Gali et al., 2017; Styszko et al., 2017, Samara, 2017)

Gali, N. K., Jiang, S. Y., Yang, F., Sun, L. and Ning, Z.: Redox characteristics of size-segregated PM from different public transport microenvironments in Hong Kong, Air Qual. Atmosphere Health, 10(7), 833–844, doi:10.1007/s11869-017-0473-0, 2017.
Styszko, K., Samek, L., Szramowiat, K., Korzeniewska, A., Kubisty, K., Rakoczy-Lelek, R., Kistler, M. and Giebl, A. K.: Oxidative potential of PM10 and PM2.5 collected at high air pollution site related to chemical composition: Krakow case study, Air Qual. Atmosphere Health, 10(9), 1123–1137, doi:10.1007/s11869-017-0499-3, 2017.

Samara, C.: On the Redox Activity of Urban Aerosol Particles: Implications for Size Distribution and Relationships with Organic Aerosol Components, Atmosphere, 8(10), 205, doi:10.3390/atmos8100205, 2017.

Pg 13 line 17. In what sense are the results very good. This is an opinion. Are the results very good because the models could reproduce the total observed Ops?
"Very good" refers to the statistical result of our inversion procedure: normalized residual distribution centered in 0, r², intercepts, uncertainties.
We replaced very good by very robust in the manuscript.

Uncertainties. A large uncertainty not considered is mixing aerosols over a broad size range into a single liquid sample and testing the OP of that mixture. These particles are definitely not internally mixed in the ambient atmosphere, nor in contact when deposited in the lung. Using PM10 makes this situation much worse as it mixes aerosol of widely different sources (secondary and mechanically generated primary, for fine and coarse, respectively). A number of papers show that there are both antagonistic and synergistic interactions possible between species that will affect the OP measurement (eg, see: Xiong, Q., H. Yu, R. Wang, J. Wei, and V. Verma (2017), Rethinking The Dithiothreitol (DTT) Based PM Oxidative Potential: Measuring DTT Consumption versus ROS Generation, Envir. Sci. Technol, 51, 6507-6514)
We perfectly agree. However, all size of particle may have health impact and then should be accounted. Moreover, a part of the coarse particle are in between the PM2.5 and PM10 (notably metals (Gietl et al., 2010)). The distinction PM10/PM2.5 and PM2.5/PM0.1 are norms and may not be fully physically based.
On top of the different size, we also consider a temporal contribution constant over the day although we know that the dynamic of some sources may vary during one day. For instance Biomass Burning is more active during evening/night and the vehicular in the morning. As a consequence, their PM may not be internally mixed neither.
We will emphasize this limitation as follows:

"An important source of uncertainty lies on the internal mixing of the aerosols as we integrate size of PM and temporal contribution of the sources. We average their contributions on a daily basis although we know that they occur at different hours of the day and with different size. As a consequence, their PM may not be internally mixed."

Gietl, J. K., Lawrence, R., Thorpe, A. J. and Harrison, R. M.: Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road, Atmospheric Environment, 44(2), 141–146, doi:10.1016/j.atmosenv.2009.10.016, 2010.

The last line of the paper needs to be edited.
"To answer these questions, more cross-over studies including OP-epidemiology and toxicology are needed."
We edited this line as follows:

"To answer these questions, more cross-over studies involving OP measurements, epidemiology and toxicology are needed."

Interactive comment on "An apportionment method for the Oxydative Potential to the atmospheric PM sources: application to a one-year study in Chamonix, France" by Samuël Weber et al.

The manuscript of Weber et al. represents the OP results obtained by analyzing a series of filter PM10 samples collected during a year-long period at an urban location in France, using two different assays, namely the dithiothreitol assay (DTT) and the ascorbic acid assay (AA). Combining results obtained by different analyses of the collected filters, including soluble ions, metals, PAHs and combining these results with PMF and linear regressions analyses for the identification of different sources and the subsequent attribution of redox-activity to different PM sources. It occurs that a large part of the observed OP is linked to biomass burning and vehicular sources for both assays. The paper is well written and easy to follow, though there are some issues and more thorough discussion should be made in specific sections. A very interesting point of the study is that the used assays appear to be sensitive to different ROS. Other than that the paper can be recommended for publication after addressing the issues listed below.

The authors would like to thank the second referee for his/her review and very useful comments that helps us to improve the paper. We tried to answer his/her question point by point in the following discussion.

1) Samples consist of PM_{10} while $PM_{2.5}$ is most commonly used as being able to penetrate inside the respiratory system. Although the used range (PM_{10}) surely covers the totality of the OP distribution, the difference of acidity between fine and coarse fraction surely plays a key role in the aerosol OP, influencing the solubility of metals (e.g. Fang et al. 2017). Authors should comment on this.

We indeed agree with the reviewer that a difference exist between PM_{10} and $PM_{2.5}$, both in term of processes influencing the OP values (like changing pH values, hence solubility of some species, according to the size), and of particle size prone to deposition in the lungs. However, in EU and France, PM_{10} are under regulation, –not $PM_{2.5}$, and are used as alert tool for health issues. Therefore, they need to be investigated with this respect.
Further, as we answered to the first reviewer, the distinctions in PM_{10}, $PM_{2.5}$ etc, are norms and are generally not be fully physically based considering the large variability of the modal size distributions observed in actual environments. Fang et al. (2017) indeed showed clear differences both for deposition of OP in respiratory tracks and in OP activity depending on the size of PM; but the threshold vary between $PM_{1.18}$ and $PM_{3.2}$, which can already make great differences in the composition of the PM compared to the $PM_{2.5}$ population. For instance, in the study by Fang et al (2017), Cu^{2+} presents its mean mass distribution value for Dp = 2.5 μm, therefore half of Cu^{2+} is in the $PM_{2.5}$ fraction, but half of it is in larger sizes.
However, we added this remark as a limitation and edited the text as follows, including also our answer to the first reviewer' comment (p14):

Even if it has been shown that mainly $PM_{2.5}$ deposit in lung alveoli (Fang et al., 2017), PM_{10} are still a public health concern and under regulation in EU and France. PM_{10} has the advantage to encompass all parts of PM potentially reaching the lower respiratory track. However, in doing so, a source of uncertainty probably arises from the mixing, in our measurements systems, of PM populations with different chemical characteristics (i.e. acidity), that can influence the OP (i.e. changing solubility of trace metal, for example).This potential artifact, already existing for $PM_{2.5}$, may be reinforced with PM_{10}.

Ting Fang, Hongyu Guo, Linghan Zeng, Vishal Verma, Athanasios Nenes, and Rodney J. Weber: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, Environmental Science & Technology 2017 51 (5), 2611-2620, DOI: 10.1021/acs.est.6b06151

2) It is stated that the current study uses simulated lung fluid (SLF) solution, complicating the direct comparison with other studies. It should be clearly stated in the abstract and conclusions section that a method different than the standard DTT protocol is used in order to avoid confusion. Furthermore, as seen in Calas et al. (2017), the OP_{DTT} measured in Milli-Q water and three different SLF extracts does not present statistically significant differences. Authors should comment on the choice of extract. Finally, in the extraction phase (P5,L13) is different extraction volume used for different samples or only a different area of the used filter? This is not clear.

We agree that we should keep in mind the difference for the extraction protocol when trying to compare studies. This comment is also shared with the first reviewer and text modification is given in our answer. We clarified the extraction protocol in the methodology part and added a paragraph in the discussion concerning the comparativeness of our solution.

However, we disagree with the term "standard DTT protocol". To the best of our knowledge, there is still no consensus toward a standardized DTT protocol. Indeed, even if Cho et al. (2005) is a general reference, several protocols have evolved from this starting one, including changes that can make large differences: removing EDTA considering its chelating effect (Charrier and Anastasio, 2012); changing the temperature of reaction and the times intervals of measurement of the kinetics ("under linear condition (DTT loss < 20%)" in Cho et al., (2005), "0, 4, 13, 23, 30 and 41 min" in Fang et al., (2015), "0, 10, 20, 30, 40 and 50 min" in Jedynska et al.,(2017), "0, 15 and 30 min" in Calas et al. (2017)) ; changing initial DTT concentrations: "160 µM" in Fujitani et al. (2017) ; "0.5 mM" in Calas et al. (2017), "1 mM" in Fang et al. (2015); "100 mM" in Jedynska et al. (2017)), etc. Moreover, it has been shown that the DTT response is not linear according to the amount of reacting species (i.e. the mass of PM) (Charrier et al., 2016), and it is definitely the main bias when comparing different studies using different PM mass extracted.

Calas et al (2018) showed that no statistical significant difference was found when using Gamble+DPPC or Milli-Q water as extraction fluids for the DTT the assay. However, in Calas et al (2018), only 5 samples were used and we clearly observed a small but constant higher OP in Milli-Q, that we explained by complexes that could take place between some species and the Gamble solution. Further, a significant difference was found between the extraction in Milli-Q water and in another lining fluid (the artificial lysosomal fluid); we did not selected this fluid for our standard protocol in our lab, since it is representative of inflammation in lung, and is therefore not relevant for all physiological conditions. As a result, we rather choose to keep the Gamble+DPPC protocol, as it is closer to biological conditions and may closely reflect the complexation occurring at the surface of lung epithelium when PM deposit.

Concerning the extraction phase, as all samples account for 24 h of sampling at constant flow rate (30 m³/h), we adjust for each sample the surface of the filter needed in order to extract always the same mass of PM (selected in the range of linearity), has it has been shown that OP_{DTT} and OP_{AA} vary non-linearly with the mass of PM in assays. We clarify this in the text, as follows:

The extraction took place into SLF at iso-mass. All samples were analyzed at 10 µg.mL^{-1} of PM, by adjusting the area of filter extracted.

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Charrier, J. G., McFall, A. S., Vu, K. K.-T., Baroi, J., Olea, C., Hasson, A. and Anastasio, C.: A bias in the mass-normalized DTT response An effect of non-linear concentration-response curves for copper and manganese, Atmospheric Environment, 144, 325 334, doi:10.1016/j.atmosenv.2016.08.071, 2016.

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Jedynska, A., Hoek, G., Wang, M., Yang, A., Eeftens, M., Cyrys, J., Keuken, M., Ampe, C., Beelen, R., Cesaroni, G., Forastiere, F., Cirach, M., de Hoogh, K., De Nazelle, A., Nystad, W., Akhlaghi, H. M., Declercq, C., Stempfelet, M., Eriksen, K. T., Dimakopoulou, K., Lanki, T., Meliefste, K., Nieuwenhuijsen, M., Yli-Tuomi, T., Raaschou-Nielsen, O., Janssen, N. A. H., Brunekreef, B. and Kooter, I. M.: Spatial variations and development of land use regression models of oxidative potential in ten European study areas, Atmospheric Environment, 150, 24 32, doi:10.1016/j.atmosenv.2016.11.029, 2017.

3) There is no mention of the LOD for the specific assays using the SLF, nor blank/blank corrections.

Indeed, this is perfectly right. The first reviewer also pointed it out. This was forgotten, and we added the following in the text :

Three filter blanks (laboratory blank) are included in every plate (OP AA and OP DTT) of the protocol. The average values of these blanks are then subtracted from the sample measurement of this plate. LOD value is defined as three times of the standard deviation of laboratory blanks measurements (blank filters in Gamble+DPPC solution).

4) When presenting the concentrations of the PMF sources, emphasis is only given for the correlation of OP solely with biomass burning and vehicular sources, even though it appears that "nitrate rich" source could also be correlated, as during winter enhanced nitrate concentrations are usually associated with biomass burning. Although mentioned further on (P12, L10) it should also be mentioned and commented on, here.

We choose to consider as "correlated" only the variables with r values above 0.6 ($p < 0,001$ for $n=85$). Thus, the correlations between OP and the nitrate rich source (Fig. S3) are below this threshold of 0.6 (resp. 0.45 and 0.55 for OP AAv and OP DTTv). This is why we do not say that this factor is correlated with OP's. However, we agree that this is an arbitrary threshold.
When we discuss it later in the text (page 10, line 11), we do not discuss about the correlation coefficient between PMF source and OP, but instead about the intrinsic OP of each source. This "low" correlation OP/PMF source but relatively high OP contribution is one of the key point of the multiple linear regression. We see that highly correlated source may have "low" intrinsic OP DTT (namely biomass burning/OP DTTv $r=0.80$ but intrinsic $OP\ DTT_{BB}=0.07$ nmol/min/μg) and poorly correlated source may have high intrinsic OP (namely Secondary biogenic/OP DTT $r=0.40$, but intrinsic $OP\ DTT_{SOA}=0.18$ nmol/min/μg). This emphasize the need of a more sophisticated statistical tool than simple univariate correlation when dealing with sources contribution to the OP.

We added the modified paragraph in the discussion:
p7, l8:

Briefly, the vehicular and biomass burning sources appear to be strongly correlated to both OP (r > 0.8). The nitrate-rich factor presents a lower correlation, as well as the sea/road salt one (0.3 < r < 0.6 for both OP's), whereas the secondary biogenic, primary biogenic, and sulfate-rich factors are slightly anti correlated with both OP's (-0.6 < r < -0.3). Crustal dust correlation is not significant with respect to the AA test but presents low correlation to the DTT test (r = 0.15 and r = 0.35, respectively).

P13 l3, we added this paragraph:

Nevertheless, all these results contrast with those from simple univariate correlations between OP and sources. Indeed, the secondary biogenic source which is slightly anti-correlated to both OP's is in fact the second most redox-active source when considering intrinsic OP_{DTT}. On the contrary, the sulfate-rich factor is slightly anti-correlated to the OP AAv but present an intrinsic OP_{AA} close to 0. The vehicular factor, which highly correlates with OP's is also the dominant source in terms of intrinsic OP's for both assays. Such results emphasize the real interest to go replace the simple univariate correlation by a more comprehensive statistical analysis when considering the contribution of the sources (or species) to the OP's.

5) A more thorough discussion should be made in the Intrinsic OP section, namely a comparison with other values found in the literature (even though the majority concerns $PM_{2.5}$) and the use or not of an intercept in the linear regression model. Furthermore, it is stated that other studies also highlight the importance of the vehicular source to explain the OP. In Verma et al. (2015) even though HOA (representing traffic) correlates

significantly with OP at some sites, the generated linear regression models do never include HOA, though in some cases the linear regression model include copper. It is known that copper may originate from brake wearing, but also it can be linked to other anthropogenic activities, such as industry and/or coal burning.

We agree that at some point a more in-depth discussion between our results and existing similar studies should be made. However, this was not the point of this paper which is focused on the methodology and only provides a case study for supporting it. An incoming study, applying this methodology to many other sites in France will be coming soon, and will compare our results to previous studies in much more details, and of course, Verma et al. (2015) will be discussed and compared in this paper.

Technical corrections:
Title: "Oxydative" should be corrected to "Oxidative"
Abstract, L1: ". . .induces cellular oxidative stress in vivo, leading to adverse. . ."
P6, L19: ". . .DTTv shows larger values. . ." (delete "has")
P7, L7: ". . .sources appear to be strongly correlated. . ."
P14, L18: "...biomass burning and vehicular sources. . ."

We would like to thank again the reviewer for his/her careful review and corrections.

An apportionment method for the ~~Oxydative~~ Oxidative Potential to the atmospheric PM sources: application to a one-year study in Chamonix, France.

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Abstract. Inhaled aerosolized particulate matter (PM) induces cellular oxidative stress in vivo ~~leads~~, leading to adverse health outcomes. The oxidative potential (OP) of PM appears to be a more relevant proxy of the health impact of the aerosol rather than the total mass concentration. However, the relative contributions of the aerosol sources to the OP are still poorly known. In order to better quantify the impact of different PM sources, we sampled aerosols in a French city for one year (year 2014, 115 samples). A coupled analysis with detailed chemical speciation (more than 100 species, including organic and carbonaceous compounds, ions, metals and Aethalometer measurements) and two OP assays (ascorbic acid (AA) and dithiothreitol (DTT)) in a simulated lung fluid (SLF) were performed in these samples. We ~~developed~~ present in this study a ~~new statistical model~~ statistical framework using a coupled approach with Positive Matrix Factorization (PMF) and multiple linear regression to attribute a redox-activity to PM sources. Our results highlight the importance of the biomass burning and vehicular sources to explain the observed OP for both assays. In general, we see a different contribution of the sources when considering the OP AA, OP DTT or the mass of the PM_{10}. Moreover, significant differences are observed between the DTT and AA tests which emphasized chemical specificities of the two tests and the need of a standardized approach for the future studies on epidemiology or toxicology of the PM.

1 Introduction

Exposure of the population to pollution by airborne particles is a growing concern due to its burden on human health, ranking as the 5th risk factor for total deaths from all causes across ages and sexes in 2015 (Cohen et al., 2017). Such impact is assessed through cross-over studies based on health data and particulate matter (PM) mass concentrations (Pope III, 2004; Pope III and Dockery, 1999; WHO, 2016). However, the dominant fraction of the PM mass are ionic species or crustal elements and these contribute little to PM toxicity (Ayres et al., 2008). Therefore, new metrics are currently investigated in order to better quantify the effect of the population exposure. Among the different metrics, oxidative potential (OP) addresses

1

the intrinsic capacity of PM to generate Reactive Oxygen Species (ROS) able to oxidize the lungs. It has been proposed as a unifying factor for quantifying the effects of particulate exposure as it relies on surface area, size and PM composition ~~(Ayres et al., 2008; Sauvain et al., 2009; Kelly and Fussell, 2012; Fang et al., 2016; Crobeddu et al., 2017; Abrams et al., 2017)~~(Ayres et a

Many methodologies to quantify OP exist, and none has become a standard so far. Since each OP methodology is somewhat specific to the precise type of ROS or ROS-inducer (Yang et al., 2014), a standard methodology should most probably include several assays in order to fully determine the ROS generation propensity (Janssen et al., 2015; Sauvain et al., 2013). Such a combination has not emerged yet, since the link between OP and chemical composition of PM is not fully understood, and OP drivers are not truly supported by evidence.

Investigating the link between OP and chemistry of PM is not simple, since particles chemical composition is unique in every sampling point. Moreover, univariate correlations can lead to false resultsr. For example, strong OP correlation with polycyclic aromatic hydrocarbon (PAH) can be found within dithiothreitol (DTT) assay (Calas et al., 2018). This correlation is chemically impossible since DTT, a reducing agent, needs redox-active compounds to be depleted (Ntziachristos et al., 2007; Shirmohammadi et al., 2016). This correlation is now well explained since PAHs are co-emitted with quinones, oxy-PAH which are redox-active and able to oxidize DTT (Charrier et al., 2015; Charrier and Anastasio, 2012). Linear multiple regression is not trivial to use in determining OP factors, since extreme outliers need to be removed, normal distributions are needed and negative contributions may be attributed to mathematically explain annual OP variations (Calas et al., 2018).

Another option is to consider the sources ~~determined by Positive Matrix Factorization (PMF) as explanatory variables (Bates et al., 2015)~~contribution instead of the chemical species (Verma et al., 2014; Bates et al., 2015; Fang et al., 2015, 2016). Indeed, working directly with chemical species involves assessing an exhaustive composition characterization. This is rather impossible since many species in the complex mixture of aerosols remain unidentified. Moreover, if a detailed composition (which can sometimes include up to 150 species (Waked et al., 2014)) is provided, at least the same number of samples for OP measurements is needed, otherwise, the system remains underdetermined. Reducing the system by direct truncation is not possible since species contributing to OP could be dropped, inducing some degree of unknown bias. Conversely, if the explanatory variables are the ~~contributions from PMF sources~~sources' contributions, biases are mitigated. ~~From seven to twelve sources are commonly extracted in PMF studies, making the system always overdetermined for most common studies, including generally a large series of samples~~However, the sources dynamics need to be determined for a long period of time in order to reflect the climatology of the location. Moreover, the composition of a given named source may vary according to its location (Belis et al., 2013). To mitigate theses issues, we decide to use a PMF approach instead of a CMB model to better render the local specificities of the sources. Indeed, the CMB averages the sources profil's from different studies and is then locally biased. Furthermore, in this study a whole year of analysis is used as input of the PMF. We then have a climatological view of the sources dynamics.

The objective of this study is to present a methodology for the evaluation of the contributions of common sources of particles to the overall OP for a long time series of PM_{10} sample (PM with a diameter lower than 10 µm). The OP was measured on filter samples collected over a full year in the city of Chamonix (Alpine valley), using two OP protocols: the ascorbic acid (AA) and dithiothreitol (DTT) assays. An inversion procedure of these OP measurements was developed using source apportionment

results obtained from an advanced source-receptor model PMF (Chevrier, 2016), in order to attribute both an intrinsic OP to the sources and the evolution of the sources contributions to OP's over the year.

2 Methods

This work takes advantage of an already existing database, based on Particulate Matter (PM_{10}) samples collected during the DECOMBIO program (Chevrier et al., 2016), with the chemical analyses and the source apportionment of PM having already been conducted (Chevrier, 2016), and the OP measurements performed on the same samples (Calas et al., 2018). These are briefly presented below.

2.1 Site and sampling

Sampling took place in the city of Chamonix-Mont-Blanc (45°55.358′ N, 6°52.194′ E), in the Alpine Arve Valley, below Mont-Blanc (Figure 1). The sampling site is located in the middle of the town, in a densely populated area, with the sampling cabin being close to a street. A one-year study was conducted from November, 14th 2013 to October, 31th 2014, with 24 hour PM_{10} sampling taking place every third day, giving a series of 115 samples. These daily PM_{10} samples were collected with a high volume sampler (Digitel, DA80, $30\,\mathrm{m^3\,h^{-1}}$) on pre-fired quartz filters (Pall, Tissuquartz). All details concerning the site and the logistical aspects of the sampling procedure can be found in Chevrier (2016).
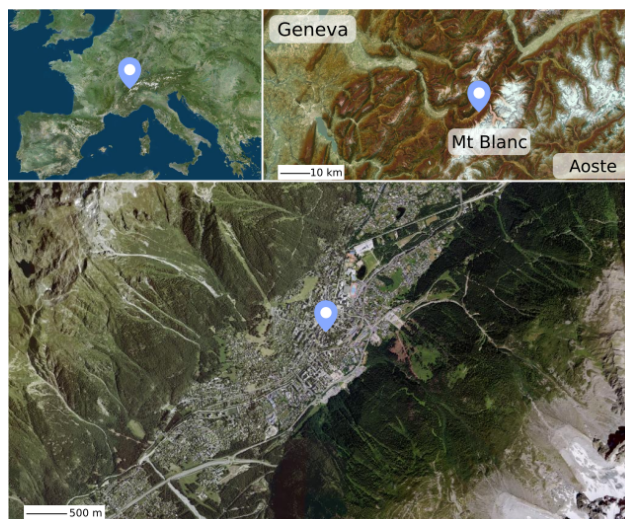

Figure 1. Location of the sampling site in Chamonix, in the Arve Valley, France (45°55.358′ N, 6°52.194′ E). © Planete observer, IGN

2.2 Chemical analyses

All filters were analyzed using a large array of methods for the quantification of chemical species including those important for the mass balance of the PM (EC, OC, ions…) and many organic and inorganic tracers of sources. The elements and components analyzed are:

- Organic and elemental carbon (OC, EC), using a Sunset instrument and the EUSAAR2 protocol (Aymoz et al., 2004; Cavalli et al., 2016);

- soluble anions and cations (NO_3^-, SO_4^{2-}, Cl^- and NH_4^+, Mg^{2+}, Na^+, Ca^{2+}, K^+) through ionic chromatography (Waked et al., 2014);

- inorganic elements (Al, Fe, Ti, As, Ba Cd, Ce, Cr, Cu, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, V, Zn and Zr) using ICP-MS (Waked et al., 2014);

- sugar alcohols (arabitol, sorbitol, and mannitol, also called polyols) and anhydrous monosaccharides (levoglucosan, mannosan and galactosan) using an HPLC-PAD method (Waked et al., 2014);

- polar and nonpolar organic tracers (alkanes, hopanes, methoxyphenols, and substituted derivatives (methyl-PAHs) and polycyclic aromatic sulfur heterocycles (PASHs) using GC-MS and polycyclic aromatic hydrocarbons (PAHs) using HPLC-fluorescence (Golly et al., 2015).

Additionally, Black Carbon (BC) measurements were ongoing throughout the year, with wood burning BC_{bb} and fossil fuel BC_{ff} fractions determined using an Athalometer AE33 and the so called "Aethalometer model" (Sandradewi et al., 2008; Drinovec et al., 2015). Although the BC measurements was performed on $PM_{2.5}$ samples, we decided to use it as Jaffrezo et al. (2005); Cavalli et al. (2016) show that the amount of EC in PM_{10} and $PM_{2.5}$ is almost equivalent.

All the procedures for these chemical analyses are described in detail in Chevrier (2016).

2.3 Source apportionment of PM_{10}

The source apportionment was performed with Positive Matrix Factorization, using the US EPA software PMF 5.0 (US EPA, 2017), following the recommendations included in the european guideline book issued in the EU Fairmode program (Belis et al., 2014). However, in the environment of Alpine valleys, the local meteorology and frequent inversion layers in winter lead to strong covariations of the concentrations of many chemical species emitted from the valley bottom. Indeed, during temperature inversion in Alpine valley, pollutants are stuck into the Atmospheric Boundary Layer (ABL) and cannot be removed by wind. Such inversion may be stable during several days. As a result, the different emission sources during that period of time add together and the dynamic from the different sources is masked. In other word, one sample does not integrate anymore only emissions during the sampling time, but also emissions of the previous days. This end-up with chemical species in one sample that should not be present together, respect to the temporality of their respective sources. Thereby, their correlation

Table 1. Selection of the chemical species used as input variables in the EPA PMF5.0 model and their relative uncertainties. Σpolyols refers to the sum of arabitol, sorbitol and mannitol and Σmethoxyphenol to the sum of the particulate methoxyphenols. The uncertainties in "%" are relative to the sample concentration for the species.

	Total	Carbonaceous matter		Ions	Organics compound		Metals
Species	PM_{10}	OC*	BC_{bb}, BC_{ff}	Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Σpolyols, MSA, levoglucosan	ΣHOP, ΣMethoxyphenol	As, Cu, Fe, Mn, Mo, Ni, Pb, Rb, Sb, Ti, V, Zn, Zr
Uncertainty	20%	10%	20%	Gianini et al. (2013)	15%	Gianini et al. (2013)	2×Gianini et al. (2013)

30   is increased. The covariation of the different pollutants adversely influences the ability of PMF to distinguish different sources. Therefore, we developed an approach including several specificities, rarely applied in classic source apportionment, in order to overcome this methodological problem in the PMF (Chevrier, 2016).

First, many tracers were included as input parameters, including specific organic tracers. The benefit of such approach was previously described (Golly, 2014; Waked et al., 2014; Srivastava et al., 2017). In our case, we included hopanes (thereafter named HOP), methoxyphenols, polyols (sum of mannitol, arabitol and sorbitol), levoglucosan and MSA (methane sulfonic acid). Instead of OC we used the difference (OC*) between the OC and the carbon equivalent of these previously analyzed species.

5   Second, elemental carbon (EC), which is an important species for the deconvolution of combustion sources was in the PMF replaced by BC_{bb} and BC_{ff} obtained using the "Aethalometer model" by concurrent measurements with the Aethalometer AE33. This provides a very strong information on the sources, as already pointed out in other studies (Petit et al., 2015). No correction was introduced to compensate between EC and BC (Zanatta et al., 2016).

Finally, we took advantage of the possibilities of PMF 5.0 to apply constraints to the factor profiles, in order to better 10   define the sources (Golly, 2014; Srivastava et al., 2017; Salameh, 2015). A minimal set of ~~geochemically sounded chemical~~ constraints based on prior and external ~~information of the source~~ geochemical knowledge of sources fingerprints was applied:

– in the biomass burning factor, the contributions of levoglucosan, potassium, methoxyphenols and BC_{bb} were ~~pulled up maximally~~increased, whereas the BC_{ff} and HOP were set to 0,

– HOP was ~~pulled up maximally~~ increased in the vehicular factor.

15   We increased the concentration of the species in the factors thanks to the "pull up maximally" option of the EPA PMF5.0 software (US EPA, 2017), which tried to increase the contribution of the given specie to the factor. Table 1 sums up the input chemistry species and respective uncertainties used in the PMF study.

2.4 Measurements of the Oxidative Potential of PM

The methodology is described in detail in Calas et al. (2017). In brief, we performed the extraction of PM into the simulated lung fluid (SLF) solution to simulate the bio-accessibility of PM and to closer simulate exposure conditions. The extraction took place into SLF ~~with the same amount of PM by mass for each sample (~~at iso-mass. All samples were analyzed at 10 µg mL^{-1} ~~)~~of PM, by adjusting the area of filter extracted. The filter extraction method includes both water soluble and insoluble species. After the SLF extraction, particles removed from filter are not filtrated; the whole extract is injected in the multiwall plate. Samples were processed using the AA and DTT assays. DTT depletion when in contact with PM extracts was determined by dosing the remaining amount of DTT with DTNB (dithionitrobenzoic acid) at different reaction times and absorbance was measured at 412 nm using a plate spectrophotometer (Tecan, M200). The AA assay is a simplified version of the synthetic respiratory tract lining fluid (RTFL) assay (Kelly and Mudway, 2003), where only AA is used. AA depletion is read continuously for 30 min from absorbance at 265 nm (TECAN, 200). The maximum depletion rate of AA is determined by linear regression of the linear section data. For both assays, the 96-wells plate is auto shaken for 3 seconds before each measurement and kept at 37 °C. Three filter blanks (laboratory blanks) are included in every plate (OP AA and OP DTT) of the protocol. The average values of these blanks are then subtracted from the sample measurement of this plate. LOD value is defined as three times of the standard deviation of laboratory blanks measurements (blank filters in Gamble+DPPC solution).

Only 98 samples out of the 115 collected were measured for OP, removing samples with insufficient PM mass concentration (<5 µg m^{-3}) that did not afford filter extraction at 10 µg mL^{-1}. The oxidative potential (OP) unit is then expressed in nmol per minute per microgram of PM. However, the population exposition is (in the first order) proportional to the mass of the inhaled PM. Therefore, the OP per microgram was multiplied by the total mass concentration of PM (µg m^{-3}) in order to express the OP in unit of nmol min^{-1} m^{-3}. We should however keep in mind that this measurement of OP may not be the exact OP from PM inhaled by the population, since we suppose a linear relationship between the OP per µg of PM and the OP of the total amount of PM. Indeed, some cocktail effects like complexation or chelation may occur for PM concentrations higher than the one tested. It has been shown by Calas et al. (2017) that the result is generally a probable over-estimation of the "true" OP. Hereafter, the OP normalized by volume is denoted with a subscribed v (OP AA$_v$ and OP DTT$_v$).

3 Results

3.1 Evolution of the OP

Both assays present a strong seasonality (Fig. 2) as already mentioned in Calas et al. (2017), and both the OP AA$_v$ and OP DTT$_v$ results show seasonality. The OP$_v$ remains high during winter and low during summer. This observation tends to emphasize the importance of PM sources which also show distinct seasonality. However, we can also observe fast variations from day to day, which may be related to a change in the PM chemistry or composition or a change in PM concentration related to sources or meteorological conditions.

Despite both assays following the same annual trend, some significant differences exist. For instance, during summer, OP DTT$_v$ ~~has~~ shows larger values, whereas the values of OP AA$_v$ are close to 0. Moreover, the variation of the OP AA$_v$ seems smoother than that of OP DTT$_v$, especially during summer and fall (May to November). This underlines that the assays are sensitive to different ~~ROS~~ chemicals species carried out by PM.
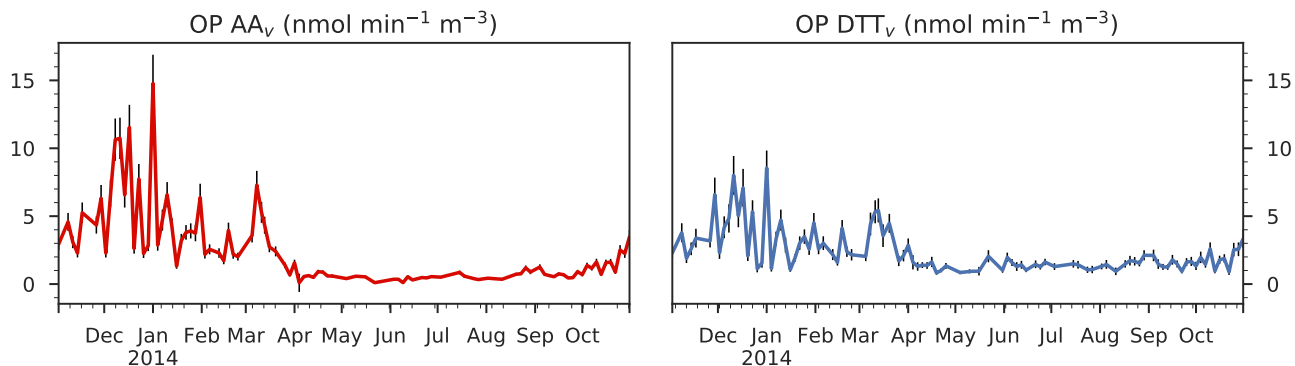

Figure 2. OP AA$_v$ and OP DTT$_v$ variation from 2 November 2013 to 31 October 2014 (98 samples) at the Chamonix station. The error bars represent the uncertainties (standard deviation) of the measurement. The OP unit is normalized by volume and is expressed in $\mathrm{nmol\,min^{-1}\,m^{-3}}$.

3.2 Evolution of the sources contributions

The PMF was already thoroughly discussed in Chevrier (2016). Briefly, 8 sources were identified: biomass burning, crustal dust, nitrate rich, sulfate rich, primary biogenic emissions an secondary biogenic aerosol, salt and vehicular emissions. Their respective main chemical species and related information are provided in the Supplementary Information (SI 1). We mainly see that metals (notably copper) and some organics species are highly correlated to both OP, together with many fractions of the carbonaceous matter (OC, BC$_{bb}$ and BC$_{ff}$, see SI 2). Figure 3 presents sources contributions to PM. The dominant PM source is biomass burning during winter with some daily concentrations exceeding $40\ \mathrm{\mu g\,m^{-3}}$. The primary and secondary biogenic sources are mainly active during summer, as is the sulfate rich source. The vehicular source is quite constant all over the year. Indeed, the higher concentration during winter may be attributed to accumulation in the ABL, and not to an increase of emission. The crustal dust contribution is sporadic and could include some Saharan episodes (Aymoz et al., 2004). Finally, the salt source is low but presents a high spike during March, being maybe related to road salting at that time of the year. The correlation between the OP and the sources are presented and discussed in the SI 2. Briefly, the vehicular and biomass burning sources ~~appears~~ appear to be strongly correlated to both OP $(r > 0.8)$. The nitrate-rich factor presents a lower correlation, as well as the sea/road salt one $(0.3 < r < 0.6$ for both OP's), whereas the secondary biogenic, primary biogenic, and sulfate-rich factors are slightly anti correlated with both OP's $(-0.6 < r < -0.3)$. Crustal dust correlation is not significant with respect to the AA test but presents low correlation to the DTT test $(r = 0.15$ and $r = 0.35$, respectively).
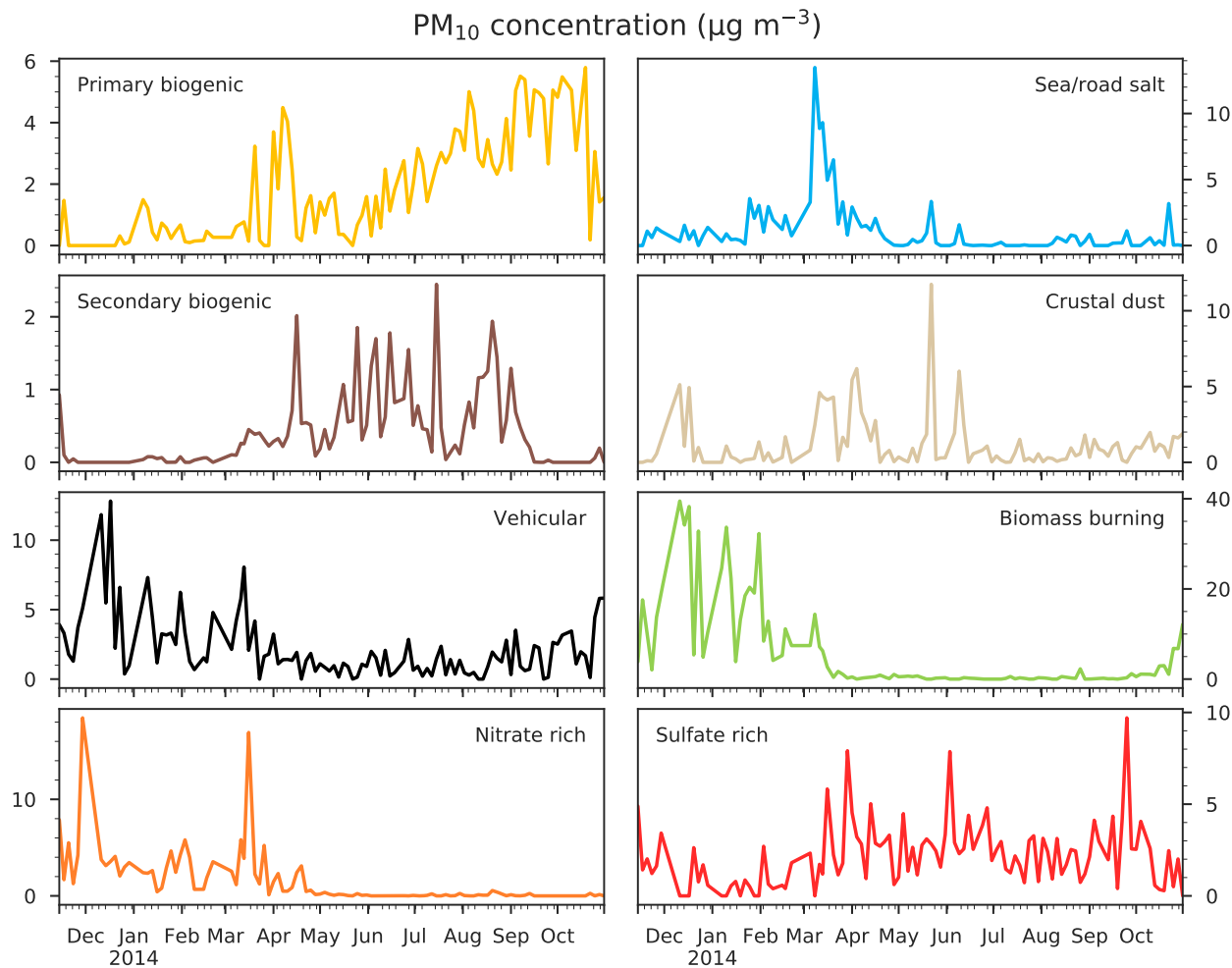
Figure 3. Mass concentrations of the eight PMF sources as fractions of PM$_{10}$ from 14 November 2013 to 31 October 2014 (107 samples) at the Chamonix station. Units are expressed in $\mu g\, m^{-3}$. Note different scales on the source contributions.

3.3 Setting up a multiple linear regression

As the OP is a value of reactivity, it cannot be directly introduced in a mass-balance model. Hence, in order to estimate the contributions of the PM sources to the OP, we must use an inversion method. Despite the possible non linearity of OP values with increasing masses of PM, as discussed below, we assume in this work that the OP is linearly linked to the mass. Thus, we hereafter assume that OP and the explanatory variables, namely the mass of the PM sources m$_{PM}$, are linearly related as follows

$$OP_{obs} = m_{PM} \cdot \beta + \varepsilon \tag{1}$$

8

where OP_{obs} is the $(n \times 1)$ observed OP matrix in $\mathrm{nmol\,min^{-1}\,m^{-3}}$, m_{PM} the $(n \times (p+1))$ matrix with the PM mass attributed to each source expressed in $\mathrm{\mu g\,m^{-3}}$ and a constant unity term with no unit for the intercept, and ε the $(n \times 1)$ uncertainty matrix in $\mathrm{nmol\,min^{-1}\,m^{-3}}$; n is the number of samples and p the number of sources. The estimator β (matrix $(p+1) \times 1$) represents the intrinsic OP of the sources (i.e. the OP per mass unit of PM attributed to a given source) and the intercept, expressed respectively in $\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for the intrinsic OP and in $\mathrm{nmol\,min^{-1}\,m^{-3}}$ for the intercept.

The optimal approximation of a solution for the linear system expressed by equation 1 is typically found by least squares. A variety of methods exist differing on the function to be minimized and on the regularization or sparsity penalty imposed to perform variable selection on β, from ordinary least squares to ridge regression and LASSO (least absolute shrinkage and selection operator). Here we have chosen a Weighted Least Squares (WLS) approach as it has an integrated way to handle the OP uncertainties. We have also chosen not to add a penalty function as we do not have prior knowledge on the intrinsic OP values. However, regular WLS do not rule out negative solutions, which should be implemented in our case since it is not demonstrated that intrinsic OP negative values exist in the real world. Therefore, a stepwise regression is conducted. The underlying algorithm is

1. Solve the WLS problem and estimate the intrinsic OP,

2. If an intrinsic OP is negative, then set it to zero and go back to step 1,

3. Repeat until all intrinsic OPs are positive or zero.

No source is discarded based on its p-value but only if its intrinsic OP is negative. We did not choose a direct non-negative least square approach as it would be a constraint in the model we believe is too strong. In addition, we can use the absence of negative coefficients as a test for the coherence of our dataset. Such approach may allow us to investigate which sources present a negative OP and why. This loop converges in a finite number of iterations, either to a situation with zero sources – which would be discarded as absurd, pointing to a breakdown of the underlying assumptions, or to an acceptable solution with a lower number of sources. In our particular case, since OP measurements never display negative values or negative source contributions from the PMF, the method is strictly guaranteed to converge to an acceptable solution. Further, we expressly do not set the intercept to zero in Eq. 1, choosing instead to use this as a check on our method. If the system is well constrained (i.e. no missing sources) the intercept should be close to zero within the model uncertainties, without any explicit constraint. The reciprocal situation could point to missing explanatory variables.

The uncertainties of the intrinsic OP are extracted from the variance of β, which in turn is derived from the Hessian matrix of the WLS regression in the standard way. However, the uncertainties on the modelled OP are not analytically computed. Indeed, some coefficients present co-variation due to the activity of the sources in the very same period of the year, so analytical variance cannot be used to estimate uncertainties. Therefore, in order to estimate the uncertainties of the modelled OP, we bootstrap the solution β 1000 times with a Monte-Carlo algorithm. The bootstrap simply selects randomly an intrinsic OP for each source according to their respective normal distribution.

The algorithm was implemented in Python 3 making use of the *statsmodels* WLS module (Seabold and Perktold, 2010).

The method proposed here is an improvement of the one of Bates et al. (2015) and our methods differ in several points. First of all, our backward elimination criteria is based on the negativity of a source and not in its p-value. Indeed, a source might present a statistically significant negative value. But according to us, a source with negative intrinsic OP does not have a geo-chemical sense as the air is known to be a strong oxidant milieu. Secondly, as Bates et al. (2015) didn't measure the uncertainty of their OP samples, they used an ordinary least square (OLS) regression. On the opposite, we have an estimation of our measurements uncertainty thanks to triplicate. We then use a weighted least square (WLS) regression instead. Finally, we propose a way to estimate uncertainties of our estimated OP with a Monte-Carlo method, which is not provided in the previous study. Moreover, the method proposed here does not only included the multiple linear regression (MLR) but also the use of the PMF model instead of the CMB one. Indeed, the MLR is highly sensitive to the explanatory variable and we decide to use the local sources' profile (PMF) instead of the chemical mass balance method with ensemble-averaged source impact profiles.

3.4 Application to the Chamonix site and discussion

Figure 4 shows the comparison between observed and modelled OPs for the measurements at the Chamonix site for both OP AA and OP DTT assays. Table 2 presents the intrinsic OP AA and OP DTT in $\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for each source with their respective uncertainties and p-values.

3.4.1 Accuracy of the model

The method developed in this study appears to be sufficiently accurate to explain the two OP annual series at Chamonix. First, the seasonal trend of the OP is very well reproduced, despite some under-estimation of some of the highest values in winter. Second, the intercept of the equation regression for OP AA_v is not significant (p>0.05). It is not so clear for the DTT test, but the p-value remains high (p=0.04). We can consider the intercepts of the equation regression as nearly negligible (see Table 2). The PM sources presented in this study are then sufficient to explain the observed OP AA_v and OP DTT_v time series. We can also note that none of the sources was excluded for the DTT assay during the inversion procedure due to negative contributions. It emphasizes the fact that the sources explain well the observed OP. However, one source was discarded for the AA assay: the crustal dust. Its p-value was less than 0.01 for an intrinsic OP of $-0.05\pm0.01\,\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$. We supposed that the crustal dust source in this study is a mixing of several sources, including Saharan dust and road suspension dust. We could then end-up with a mixing of highly different redox-active compounds towards AA test that could explain the error for this source. Further work is needed to understand this behavior.

3.4.2 Uncertainties and residual

The uncertainties of the modeled OP are quite low and mostly in the range of the measurement uncertainties (Figure 4). Indeed, the distribution of the residual is close to the normal law (Figure 5). However, we can note an asymmetry toward underestimation and residual seem to increase almost linearly with the endogenous variable (no random repartition around 0

30 for the highest OP). The OP is underestimated by the model for these days featuring concentrations. It may suggest either non-linearity with high loading (as suggested above), or particular event that is not apportioned by the sources provided in this study.
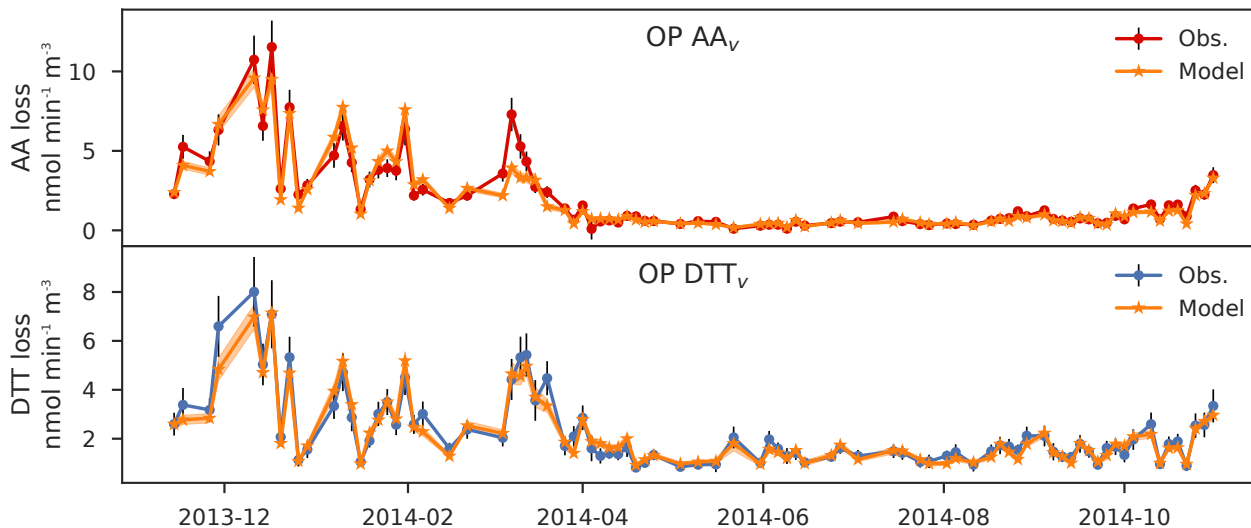

Figure 4. Comparison of the modelled OP (orange) and the observed OP for both the AA (top graph) and DTT (bottom graph) test (85 samples) from November 2013 to November 2014. The black error bars are the standard deviation of the observed values and the shaded orange area the uncertainties of the modelled OP. Units are in OP normalized by volume and expressed in $\mathrm{nmol\,min^{-1}\,m^{-3}}$.

3.4.3 Intrinsic OP

Values of the intrinsic OP of different sources for both the AA and DTT assays are ranging from zero to $0.18\pm0.01\,\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$
5 for the AA test and from $0.06\pm0.02\,\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ to $0.27\pm0.03\,\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for the DTT test (Table 2). The various sources do not have the same ~~ability to generate ROS~~reactivity toward the AA and DTT. We also note that the two tests present different intrinsic OP for the same source, and the relative importance of the sources differs from one test to the other. For instance, the vehicular source displays a lower intrinsic OP ($0.15\,\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$) than the biomass burning ($0.18\,\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$) for the AA test but a higher intrinsic OP for the DTT test ($0.27\,\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for the vehicular
10 and $0.07\,\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for the biomass burning). This deconvolution method may be able to account for the chemical specificity of the two OP assays. In addition, the DTT test seems to be more multi-sources influenced than the AA test.

Nevertheless, we clearly see the importance of the vehicular source, which is associated to a strong intrinsic OP in both the AA and DTT assays. Previous studies (Bates et al., 2015; Fang et al., 2016; Verma et al., 2014) also highlighted the importance of this source to explain the OP AA and DTT. We may explain such high intrinsic OP by the presence of metals in this source
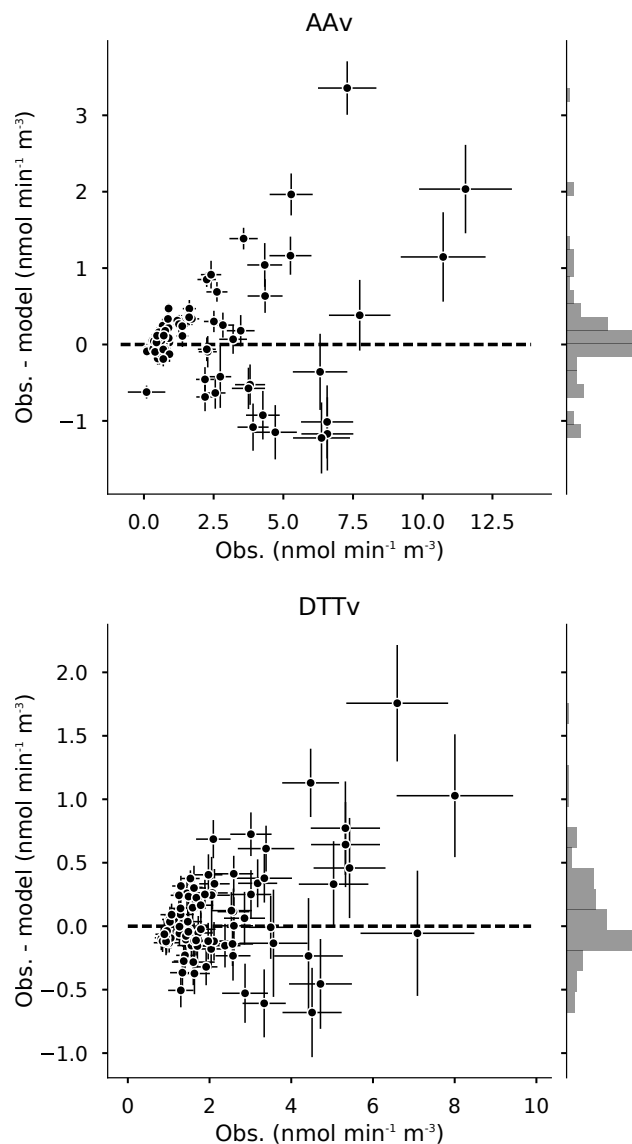15 – notably the copper (Charrier et al., 2015).

Figure 5. Residual distribution for the regression of the AA and DTT assays (85 samples). The error bars represent the standard deviation of the observation and the model. The histogram on the right is the distribution of the residuals. Units are in OP normalized by volume and expressed in $\mathrm{nmol\,min^{-1}\,m^{-3}}$. Note different scales for the AA_v and the DTT_v.

In the AA assay, the biomass burning also presents a high redox-activity per µg of PM. This result disagrees with Fang et al. (2016) as they found no activity for this source in the OP AA test. Such difference for the biomass burning source may be explained by the two extraction protocols (in water or in a SLF solution) or by the proximity of the biomass source in Chamonix compared to the longer distance transport in Atlanta, that would change the chemistry of the source profile. However, the biomass burning in the OP DTT test has an intrinsic OP of $0.07\pm0.01\ \mathrm{nmol\,min^{-1}\,m^{-3}}$, which is coherent with

Table 2. Regression coefficients (i.e. intrinsic OP) expressed in $\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ at Chamonix for the AA and DTT assays. The values are the mean±standard deviation based on N=1000 bootstrap of the best solution. The p-value is in the parenthesis. The crustal dust source was excluded during the inversion process for the AA test.

	Biomass burning	Crustal dust	Nitrate rich	Primary biogenic	Sea/road salt	Secondary biogenic	Sulfate rich	Vehicular	Intercept
Unit				$\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$					$\mathrm{nmol\,min^{-1}\,m^{-3}}$
AA	0.18±0.01	-	0.12±0.02	0.07±0.01	0.03±0.01	0.02±0.04	0.00±0.01	0.15±0.02	0.05±0.08
	(<0.001)	(-)	(<0.001)	(<0.001)	(0.140)	(0.598)	(0.942)	(<0.001)	(0.502)
DTT	0.07±0.01	0.07±0.02	0.07±0.02	0.12±0.02	0.14±0.03	0.18±0.05	0.06±0.02	0.27±0.03	0.17±0.08
	(<0.001)	(0.003)	(<0.001)	(<0.001)	(<0.001)	(<0.001)	(<0.001)	(<0.001)	(0.045)

the previous study of Fang et al. (2016). The presence of oxygenated compounds such as quinones which are redox-active in the organic matter could explain this high intrinsic OP.

The nitrate-rich source also appears to contribute in the redox-activity in both assays. Although the nitrate itself is not redox-active, it can be present with species that are oxidants. More work is needed in order to understand the evolution of intrinsic OP for the nitrate rich factor, including measurements on series characterized by specific spring events related to agricultural activities, and series close to traffic sites for NO_x emissions.

The primary biogenic source, mainly identified by the presence of polyols, presents a significant intrinsic OP. This result was unexpected. Indeed, Liu et al. (2010) shows that mannitol is a strong anti-oxidant. Our result suggests that some chemical species, present in the primary biogenic source but not measured in this study, may contribute to the OP of the PM from this source. Recently, it was shown that fungal spores exhibit a significant intrinsic OP (Samake et al., 2017), and this may be an hypothesis to be further tested. However, the PMF profile of the primary biogenic source may also be a mixing of different sources in our study (there is BC_{ff} in it for instance). Such mixing may also explain the high intrinsic OP of this source.

Nevertheless, all these results contrast with those from simple univariate correlations between OP and sources. Indeed, the secondary biogenic source which is slightly anti-correlated to both OP's is in fact the second most redox-active source when considering intrinsic OP DTT. On the contrary, the sulfate-rich factor is slightly anti-correlated to the OP AA_v but present an intrinsic OP AA close to 0. The vehicular factor, which highly correlates with OP's is also the dominant source in terms of intrinsic OP's for both assays. Such results emphasize the real interest to go replace the simple univariate correlation by a more comprehensive statistical analysis when considering the contribution of the sources (or species) to the OP's.

3.4.4 Contribution to the OP

The aim of this study was to establish a deconvolution model for the OP. The results obtained with it will be discussed in depth in another study, including other sites. However, here are some preliminary results for the Chamonix station concerning the sources contribution.

Due to the different intrinsic OP of the sources, the source contributions to the OP (intrinsic OP times by the source contribution in $\mu g\,m^{-3}$) is different from their contribution to the PM mass. Figure 6 illustrates the normalized contribution of the sources to the mass of the aerosols and the OP measures with AA and DTT. It shows that the vehicular source barely contributes to 17 % of the total PM mass during March-April-May (MAM) and June-July-August (JJA) but more than 30 % to the OP DTT_v in the same period, and even reaching around 50 % of the OP AA_v in JJA. Conversely, some sources largely contributing to the PM_{10} mass such as the sulfate-rich source (30 % of the total PM mass in JJA) do not contribute to the OP (2 % to the OP AA_v in the same period). Finally, some sources like the biomass burning contribute to a large extend in both PM mass and OP (on an annual basis: 35 % of the PM mass, 55 % of the OP AA_v and 22 % of the OP DTT_v). We also note that on an annual basis, the contribution of the vehicular source is much larger for both OP assays than for the mass. All these outcomes are key parameters for policy initiatives.

To sum up, with this methodology, we observe a redistribution of the relative importance of the sources ranked as ROS contributors. This study gives, and more generally, the OP gives us a new vision of the atmospheric aerosols and associated ROS burden. We also point out a clear distinction between the different OP tests. Such differences raise new questions on OP assays choices and standardization and require further investigation, especially coupled OP-toxicology-epidemiology studies.
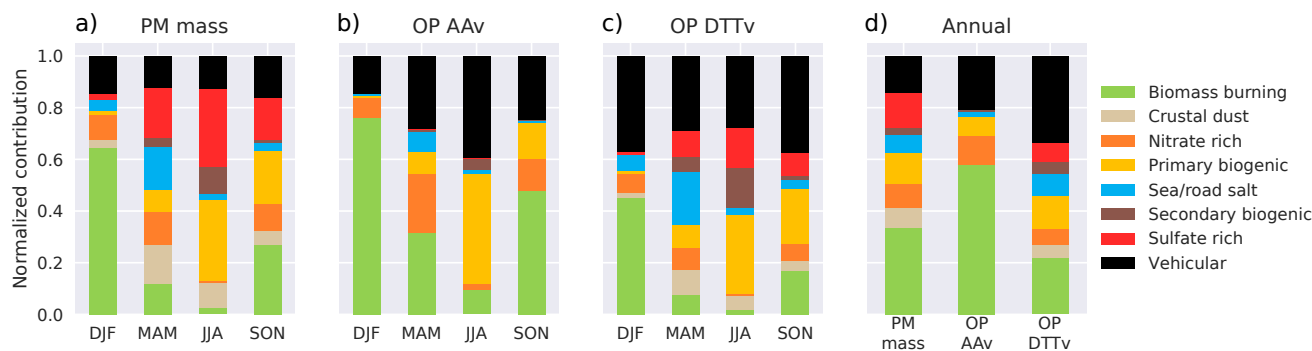

Figure 6. Normalized seasonal contribution of the sources to a) the PM_{10} total mass, b) the OP AA_v and c) the OP DTT_v. DJF is December-January-February, MAM is March-April-May, JJA is June-July-August and SON is September-October-November. d) annual normalized contributions of each source to the PM, OP AAv and OP DTTv.

4 Limitations

First of all, when comparing with others previous studies we should note that our PM extraction of samples were done in a SLF and not in water. This induces a difference in OP measurement which is not predictable for the complexes occurring between PM and SLF compounds as when PM enters in contact with the epithelial lung fluid (Calas et al., 2017) and then direct comparison may not be fully accurate.

The method used in this study gives very ~~good~~ robust results and is promising for practical application. However, since it has some limitations, we hereafter list some possible improvements. First, as previously discussed, the model is strongly

14

constrained by the explanatory variable, which are the PM sources contributions obtained with a PMF analysis. The PMF model has uncertainties of two different natures, inherent to the model: 1) mathematical uncertainties on the sources contributions and 2) frequent mixing profiles, due to co-linearity induced, e.g., mainly by meteorology. In our study, we might encounter such mixing for the biogenic sources. An improvement would be to bootstrap the PMF results and use these uncertainties in the OP

5   inversion in order to see its sensitivity.

Even if it has been shown that mainly $PM_{2.5}$ deposit in lung alveoli (Fang et al., 2017), PM_{10} are still a public health concern and under regulation in EU and France. PM_{10} has the advantage to encompass all parts of PM potentially reaching the lower respiratory track. However, in doing so, a source of uncertainty probably arises from the mixing, in our measurements systems, of PM populations with different chemical characteristics (i.e. acidity), that can influence the OP (i.e. changing solubility of

10   trace metal, for example).This potential artifact, already existing for $PM_{2.5}$, may be reinforced with PM_{10}.

Another debatable choice is setting the intrinsic OP to zero for the source with a negative intrinsic OP during the stepwise regression process. Some chemical species may act as anti-oxidants which lead to "negative" intrinsic OP for the associated PM source. Namely, the polyols from the primary biogenic source, that include species like mannitol, are known to present strong anti-oxidant capabilities (Liu et al., 2010) and bacteria can halve the OP of copper-rich PM (Samake et al., 2017).

15   Further studies should focus on this topic in order to better understand this potential effect.

Other choices of targets for optimization, and of penalty functions to promote the positivity of the coefficients, are possible. However, we think that our proposals manage to strike a balance between a satisfactory handling of the uncertainties of the problem and ease of application using existing statistical frameworks.

5   Conclusions

20   Based on one-year PM_{10} sampling at an urban site located in Chamonix (France) associated with chemical speciation and Oxidative Potential (OP) measurements with the DTT and OP AA assays, we successfully established a method to attribute the contribution of the PM sources to the observed OP. The main ~~conlusions~~ conclusions of this study are summarized hereafter:

1. The different sources present different OP AA and OP DTT per microgram of PM with intrinsic OP differences between sources up to a factor of 20.

25   2. The biomass burning and ~~Vvhicular~~ vehicular sources seem to be the leading sources of the OP AA_v and OP DTT_v in Chamonix. On an annual basis, they represent together 78 % of the OP AA_v and 54 % of the OP DTT_v apportionment.

3. The two OP ~~essays~~ assays present different view on the PM sources based on their specific chemical selectivity as illustrated by the salt source that does not contribute to the OP AA_v but to the OP DTT_v.

4. The relative mass contributions of the sources to the PM_{10} differ from their relative OP AA_v and OP DTT_v contributions. For instance, the vehicular source has a larger contribution to the total OP AA and OP DTT than to the total PM_{10} mass, whereas the sulfate rich source appears to be a minor source of OP AA_v but an important source of PM mass. If OP is a

proper metric of health impact of PM on population, the PM mass is not fully appropriate for PM regulations targeting public health.

5   Finally, even if OP metric is correlated to health outcomes, this study cannot directly attribute toxicity to one source or another. Is sporadic exposure to PM with high OP values or chronical exposure to PM with low OP values sufficient to provoke health damage? As the DTT and AA tests point different sources as the main ROS-generating, does one of them is the more linked to toxicological effects (if any)? To answer these questions, more cross-over studies ~~including OP-epidemiology~~ involving OP measurements, epidemiology and toxicology are needed.

16

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An apportionment method for the ~~Oxydative~~ Oxidative Potential to the atmospheric PM sources: application to a one-year study in Chamonix, France.

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Abstract. Inhaled aerosolized particulate matter (PM) induces cellular oxidative stress in vivo ~~leads~~, leading to adverse health outcomes. The oxidative potential (OP) of PM appears to be a more relevant proxy of the health impact of the aerosol rather than the total mass concentration. However, the relative contributions of the aerosol sources to the OP are still poorly known. In order to better quantify the impact of different PM sources, we sampled aerosols in a French city for one year (year 2014, 115 samples). A coupled analysis with detailed chemical speciation (more than 100 species, including organic and carbonaceous compounds, ions, metals and Aethalometer measurements) and two OP assays (ascorbic acid (AA) and dithiothreitol (DTT)) in a simulated lung fluid (SLF) were performed in these samples. We ~~developed~~ present in this study a ~~new statistical model~~ statistical framework using a coupled approach with Positive Matrix Factorization (PMF) and multiple linear regression to attribute a redox-activity to PM sources. Our results highlight the importance of the biomass burning and vehicular sources to explain the observed OP for both assays. In general, we see a different contribution of the sources when considering the OP AA, OP DTT or the mass of the PM_{10}. Moreover, significant differences are observed between the DTT and AA tests which emphasized chemical specificities of the two tests and the need of a standardized approach for the future studies on epidemiology or toxicology of the PM.

1   Introduction

Exposure of the population to pollution by airborne particles is a growing concern due to its burden on human health, ranking as the 5th risk factor for total deaths from all causes across ages and sexes in 2015 (Cohen et al., 2017). Such impact is assessed through cross-over studies based on health data and particulate matter (PM) mass concentrations (Pope III, 2004; Pope III and Dockery, 1999; WHO, 2016). However, the dominant fraction of the PM mass are ionic species or crustal elements and these contribute little to PM toxicity (Ayres et al., 2008). Therefore, new metrics are currently investigated in order to better quantify the effect of the population exposure. Among the different metrics, oxidative potential (OP) addresses

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the intrinsic capacity of PM to generate Reactive Oxygen Species (ROS) able to oxidize the lungs. It has been proposed as a unifying factor for quantifying the effects of particulate exposure as it relies on surface area, size and PM composition ~~(Ayres et al., 2008; Sauvain et al., 2009; Kelly and Fussell, 2012; Fang et al., 2016; Crobeddu et al., 2017; Abrams et al., 2017)~~(Ayres et a

Many methodologies to quantify OP exist, and none has become a standard so far. Since each OP methodology is somewhat specific to the precise type of ROS or ROS-inducer (Yang et al., 2014), a standard methodology should most probably include several assays in order to fully determine the ROS generation propensity (Janssen et al., 2015; Sauvain et al., 2013). Such a combination has not emerged yet, since the link between OP and chemical composition of PM is not fully understood, and OP drivers are not truly supported by evidence.

Investigating the link between OP and chemistry of PM is not simple, since particles chemical composition is unique in every sampling point. Moreover, univariate correlations can lead to false resultsr. For example, strong OP correlation with polycyclic aromatic hydrocarbon (PAH) can be found within dithiothreitol (DTT) assay (Calas et al., 2018). This correlation is chemically impossible since DTT, a reducing agent, needs redox-active compounds to be depleted (Ntziachristos et al., 2007; Shirmohammadi et al., 2016). This correlation is now well explained since PAHs are co-emitted with quinones, oxy-PAH which are redox-active and able to oxidize DTT (Charrier et al., 2015; Charrier and Anastasio, 2012). Linear multiple regression is not trivial to use in determining OP factors, since extreme outliers need to be removed, normal distributions are needed and negative contributions may be attributed to mathematically explain annual OP variations (Calas et al., 2018).

Another option is to consider the sources ~~determined by Positive Matrix Factorization (PMF) as explanatory variables (Bates et al., 2015)~~contribution instead of the chemical species (Verma et al., 2014; Bates et al., 2015; Fang et al., 2015, 2016). Indeed, working directly with chemical species involves assessing an exhaustive composition characterization. This is rather impossible since many species in the complex mixture of aerosols remain unidentified. Moreover, if a detailed composition (which can sometimes include up to 150 species (Waked et al., 2014)) is provided, at least the same number of samples for OP measurements is needed, otherwise, the system remains underdetermined. Reducing the system by direct truncation is not possible since species contributing to OP could be dropped, inducing some degree of unknown bias. Conversely, if the explanatory variables are the ~~contributions from PMF sources~~sources' contributions, biases are mitigated. ~~From seven to twelve sources are commonly extracted in PMF studies, making the system always overdetermined for most common studies, including generally a large series of samples~~However, the sources dynamics need to be determined for a long period of time in order to reflect the climatology of the location. Moreover, the composition of a given named source may vary according to its location (Belis et al., 2013). To mitigate theses issues, we decide to use a PMF approach instead of a CMB model to better render the local specificities of the sources. Indeed, the CMB averages the sources profil's from different studies and is then locally biased. Furthermore, in this study a whole year of analysis is used as input of the PMF. We then have a climatological view of the sources dynamics.

The objective of this study is to present a methodology for the evaluation of the contributions of common sources of particles to the overall OP for a long time series of PM_{10} sample (PM with a diameter lower than 10 µm). The OP was measured on filter samples collected over a full year in the city of Chamonix (Alpine valley), using two OP protocols: the ascorbic acid (AA) and dithiothreitol (DTT) assays. An inversion procedure of these OP measurements was developed using source apportionment

results obtained from an advanced source-receptor model PMF (Chevrier, 2016), in order to attribute both an intrinsic OP to the sources and the evolution of the sources contributions to OP's over the year.

2   Methods

This work takes advantage of an already existing database, based on Particulate Matter (PM_{10}) samples collected during the DECOMBIO program (Chevrier et al., 2016), with the chemical analyses and the source apportionment of PM having already been conducted (Chevrier, 2016), and the OP measurements performed on the same samples (Calas et al., 2018). These are briefly presented below.

2.1   Site and sampling

Sampling took place in the city of Chamonix-Mont-Blanc (45°55.358′ N, 6°52.194′ E), in the Alpine Arve Valley, below Mont-Blanc (Figure 1). The sampling site is located in the middle of the town, in a densely populated area, with the sampling cabin being close to a street. A one-year study was conducted from November, 14th 2013 to October, 31th 2014, with 24 hour PM_{10} sampling taking place every third day, giving a series of 115 samples. These daily PM_{10} samples were collected with a high volume sampler (Digitel, DA80, 30 $\mathrm{m^3\,h^{-1}}$) on pre-fired quartz filters (Pall, Tissuquartz). All details concerning the site and the logistical aspects of the sampling procedure can be found in Chevrier (2016).
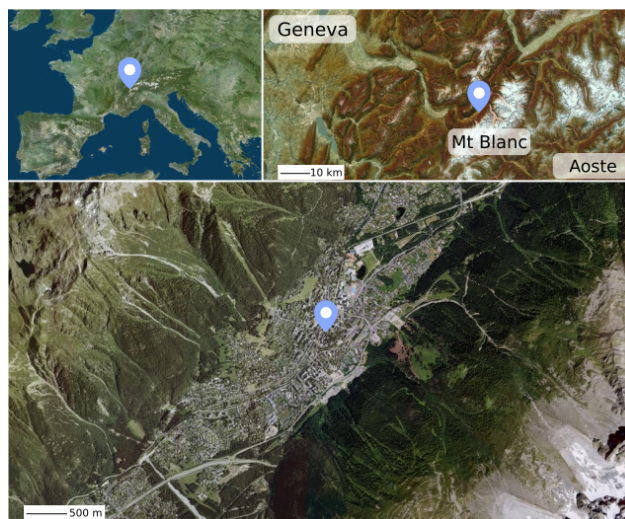

Figure 1. Location of the sampling site in Chamonix, in the Arve Valley, France (45°55.358′ N, 6°52.194′ E). © Planete observer, IGN

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2.2 Chemical analyses

All filters were analyzed using a large array of methods for the quantification of chemical species including those important for the mass balance of the PM (EC, OC, ions...) and many organic and inorganic tracers of sources. The elements and components analyzed are:

- Organic and elemental carbon (OC, EC), using a Sunset instrument and the EUSAAR2 protocol (Aymoz et al., 2004; Cavalli et al., 2016);

- soluble anions and cations (NO_3^-, SO_4^{2-}, Cl^- and NH_4^+, Mg^{2+}, Na^+, Ca^{2+}, K^+) through ionic chromatography (Waked et al., 2014);

- inorganic elements (Al, Fe, Ti, As, Ba Cd, Ce, Cr, Cu, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, V, Zn and Zr) using ICP-MS (Waked et al., 2014);

- sugar alcohols (arabitol, sorbitol, and mannitol, also called polyols) and anhydrous monosaccharides (levoglucosan, mannosan and galactosan) using an HPLC-PAD method (Waked et al., 2014);

- polar and nonpolar organic tracers (alkanes, hopanes, methoxyphenols, and substituted derivatives (methyl-PAHs) and polycyclic aromatic sulfur heterocycles (PASHs) using GC-MS and polycyclic aromatic hydrocarbons (PAHs) using HPLC-fluorescence (Golly et al., 2015).

Additionally, Black Carbon (BC) measurements were ongoing throughout the year, with wood burning BC_{bb} and fossil fuel BC_{ff} fractions determined using an Athalometer AE33 and the so called "Aethalometer model" (Sandradewi et al., 2008; Drinovec et al., 2015). Although the BC measurements was performed on $PM_{2.5}$ samples, we decided to use it as Jaffrezo et al. (2005); Cavalli et al. (2016) show that the amount of EC in PM_{10} and $PM_{2.5}$ is almost equivalent.

All the procedures for these chemical analyses are described in detail in Chevrier (2016).

2.3 Source apportionment of PM_{10}

The source apportionment was performed with Positive Matrix Factorization, using the US EPA software PMF 5.0 (US EPA, 2017), following the recommendations included in the european guideline book issued in the EU Fairmode program (Belis et al., 2014). However, in the environment of Alpine valleys, the local meteorology and frequent inversion layers in winter lead to strong covariations of the concentrations of many chemical species emitted from the valley bottom. Indeed, during temperature inversion in Alpine valley, pollutants are stuck into the Atmospheric Boundary Layer (ABL) and cannot be removed by wind. Such inversion may be stable during several days. As a result, the different emission sources during that period of time add together and the dynamic from the different sources is masked. In other word, one sample does not integrate anymore only emissions during the sampling time, but also emissions of the previous days. This end-up with chemical species in one sample that should not be present together, respect to the temporality of their respective sources. Thereby, their correlation

Table 1. Selection of the chemical species used as input variables in the EPA PMF5.0 model and their relative uncertainties. Σpolyols refers to the sum of arabitol, sorbitol and mannitol and Σmethoxyphenol to the sum of the particulate methoxyphenols. The uncertainties in "%" are relative to the sample concentration for the species.

	Total	Carbonaceous matter		Ions	Organics compound		Metals
Species	PM$_{10}$	OC*	BC$_{bb}$, BC$_{ff}$	Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}	Σpolyols, MSA, levoglucosan	ΣHOP, ΣMethoxyphenol	As, Cu, Fe, Mn, Mo, Ni, Pb, Rb, Sb, Ti, V, Zn, Zr
Uncertainty	20%	10%	20%	Gianini et al. (2013)	15%	Gianini et al. (2013)	2×Gianini et al. (2013)

30 is increased. The covariation of the different pollutants adversely influences the ability of PMF to distinguish different sources. Therefore, we developed an approach including several specificities, rarely applied in classic source apportionment, in order to overcome this methodological problem in the PMF (Chevrier, 2016).

First, many tracers were included as input parameters, including specific organic tracers. The benefit of such approach was previously described (Golly, 2014; Waked et al., 2014; Srivastava et al., 2017). In our case, we included hopanes (thereafter named HOP), methoxyphenols, polyols (sum of mannitol, arabitol and sorbitol), levoglucosan and MSA (methane sulfonic acid). Instead of OC we used the difference (OC*) between the OC and the carbon equivalent of these previously analyzed species.

5 Second, elemental carbon (EC), which is an important species for the deconvolution of combustion sources was in the PMF replaced by BC$_{bb}$ and BC$_{ff}$ obtained using the "Aethalometer model" by concurrent measurements with the Aethalometer AE33. This provides a very strong information on the sources, as already pointed out in other studies (Petit et al., 2015). No correction was introduced to compensate between EC and BC (Zanatta et al., 2016).

Finally, we took advantage of the possibilities of PMF 5.0 to apply constraints to the factor profiles, in order to better

10 define the sources (Golly, 2014; Srivastava et al., 2017; Salameh, 2015). A minimal set of ~~geochemically sounded chemical~~ constraints based on prior and external ~~information of the source~~ geochemical knowledge of sources fingerprints was applied:

- in the biomass burning factor, the contributions of levoglucosan, potassium, methoxyphenols and BC$_{bb}$ were ~~pulled up maximally~~increased, whereas the BC$_{ff}$ and HOP were set to 0,

- HOP was ~~pulled up maximally~~ increased in the vehicular factor.

15 We increased the concentration of the species in the factors thanks to the "pull up maximally" option of the EPA PMF5.0 software (US EPA, 2017), which tried to increase the contribution of the given specie to the factor. Table 1 sums up the input chemistry species and respective uncertainties used in the PMF study.

2.4 Measurements of the Oxidative Potential of PM

The methodology is described in detail in Calas et al. (2017). In brief, we performed the extraction of PM into the simulated lung fluid (SLF) solution to simulate the bio-accessibility of PM and to closer simulate exposure conditions. The extraction took place into SLF ~~with the same amount of PM by mass for each sample (~~at iso-mass. All samples were analyzed at 10 µg mL^{-1} ~~)~~of PM, by adjusting the area of filter extracted. The filter extraction method includes both water soluble and insoluble species. After the SLF extraction, particles removed from filter are not filtrated; the whole extract is injected in the multiwall plate. Samples were processed using the AA and DTT assays. DTT depletion when in contact with PM extracts was determined by dosing the remaining amount of DTT with DTNB (dithionitrobenzoic acid) at different reaction times and absorbance was measured at 412 nm using a plate spectrophotometer (Tecan, M200). The AA assay is a simplified version of the synthetic respiratory tract lining fluid (RTFL) assay (Kelly and Mudway, 2003), where only AA is used. AA depletion is read continuously for 30 min from absorbance at 265 nm (TECAN, 200). The maximum depletion rate of AA is determined by linear regression of the linear section data. For both assays, the 96-wells plate is auto shaken for 3 seconds before each measurement and kept at 37 °C. Three filter blanks (laboratory blanks) are included in every plate (OP AA and OP DTT) of the protocol. The average values of these blanks are then subtracted from the sample measurement of this plate. LOD value is defined as three times of the standard deviation of laboratory blanks measurements (blank filters in Gamble+DPPC solution).

Only 98 samples out of the 115 collected were measured for OP, removing samples with insufficient PM mass concentration (<5 µg m^{-3}) that did not afford filter extraction at 10 µg mL^{-1}. The oxidative potential (OP) unit is then expressed in nmol per minute per microgram of PM. However, the population exposition is (in the first order) proportional to the mass of the inhaled PM. Therefore, the OP per microgram was multiplied by the total mass concentration of PM (µg m^{-3}) in order to express the OP in unit of nmol min^{-1} m^{-3}. We should however keep in mind that this measurement of OP may not be the exact OP from PM inhaled by the population, since we suppose a linear relationship between the OP per µg of PM and the OP of the total amount of PM. Indeed, some cocktail effects like complexation or chelation may occur for PM concentrations higher than the one tested. It has been shown by Calas et al. (2017) that the result is generally a probable over-estimation of the "true" OP. Hereafter, the OP normalized by volume is denoted with a subscribed v (OP AA$_v$ and OP DTT$_v$).

3 Results

3.1 Evolution of the OP

Both assays present a strong seasonality (Fig. 2) as already mentioned in Calas et al. (2017), and both the OP AA$_v$ and OP DTT$_v$ results show seasonality. The OP$_v$ remains high during winter and low during summer. This observation tends to emphasize the importance of PM sources which also show distinct seasonality. However, we can also observe fast variations from day to day, which may be related to a change in the PM chemistry or composition or a change in PM concentration related to sources or meteorological conditions.

Despite both assays following the same annual trend, some significant differences exist. For instance, during summer, OP DTT$_v$ ~~has~~ shows larger values, whereas the values of OP AA$_v$ are close to 0. Moreover, the variation of the OP AA$_v$ seems smoother than that of OP DTT$_v$, especially during summer and fall (May to November). This underlines that the assays are

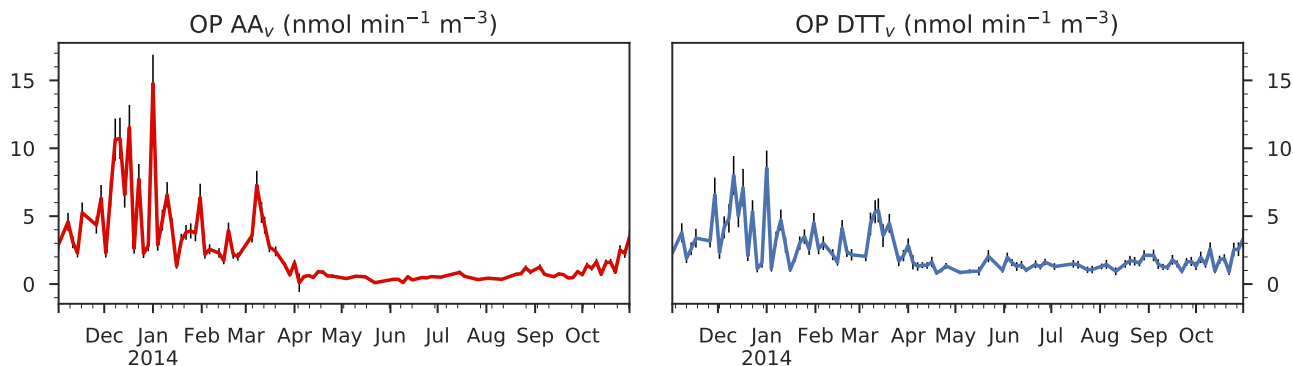30 sensitive to different ~~ROS~~ chemicals species carried out by PM.

Figure 2. OP AA$_v$ and OP DTT$_v$ variation from 2 November 2013 to 31 October 2014 (98 samples) at the Chamonix station. The error bars represent the uncertainties (standard deviation) of the measurement. The OP unit is normalized by volume and is expressed in $\mathrm{nmol\,min^{-1}\,m^{-3}}$.

3.2   Evolution of the sources contributions

The PMF was already thoroughly discussed in Chevrier (2016). Briefly, 8 sources were identified: biomass burning, crustal dust, nitrate rich, sulfate rich, primary biogenic emissions an secondary biogenic aerosol, salt and vehicular emissions. Their respective main chemical species and related information are provided in the Supplementary Information (SI 1). We mainly see that metals (notably copper) and some organics species are highly correlated to both OP, together with many fractions of

5 the carbonaceous matter (OC, BC$_{bb}$ and BC$_{ff}$, see SI 2). Figure 3 presents sources contributions to PM. The dominant PM source is biomass burning during winter with some daily concentrations exceeding $40\ \mathrm{\mu g\,m^{-3}}$. The primary and secondary biogenic sources are mainly active during summer, as is the sulfate rich source. The vehicular source is quite constant all over the year. Indeed, the higher concentration during winter may be attributed to accumulation in the ABL, and not to an increase of emission. The crustal dust contribution is sporadic and could include some Saharan episodes (Aymoz et al., 2004). Finally,

10 the salt source is low but presents a high spike during March, being maybe related to road salting at that time of the year. The correlation between the OP and the sources are presented and discussed in the SI 2. Briefly, the vehicular and biomass burning sources ~~appears~~ appear to be strongly correlated to both OP ($r > 0.8$). The nitrate-rich factor presents a lower correlation, as well as the sea/road salt one ($0.3 < r < 0.6$ for both OP's), whereas the secondary biogenic, primary biogenic, and sulfate-rich factors are slightly anti correlated with both OP's ($-0.6 < r < -0.3$). Crustal dust correlation is not significant with respect to

15 the AA test but presents low correlation to the DTT test ($r = 0.15$ and $r = 0.35$, respectively).
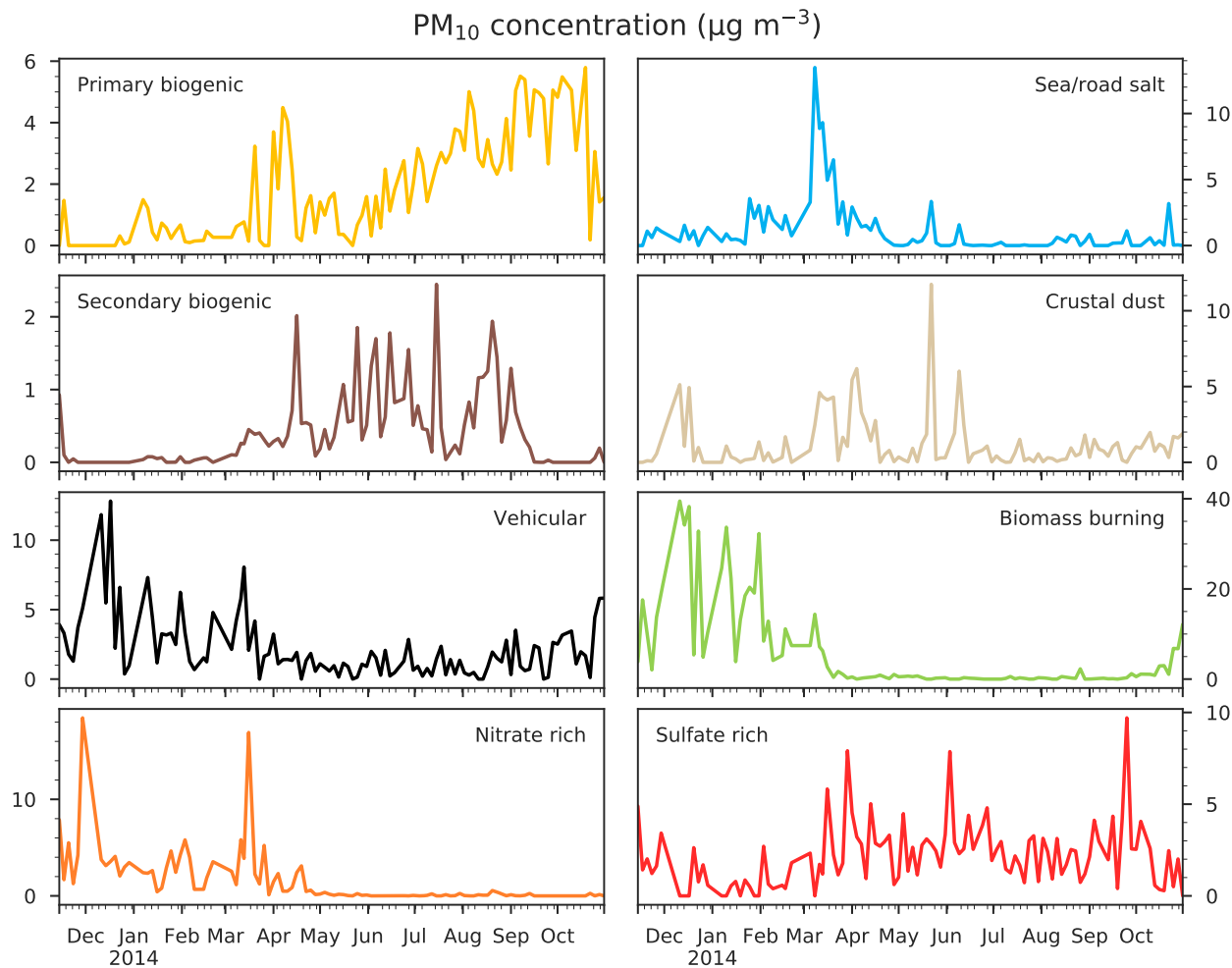
Figure 3. Mass concentrations of the eight PMF sources as fractions of PM_{10} from 14 November 2013 to 31 October 2014 (107 samples) at the Chamonix station. Units are expressed in $\mu g\,m^{-3}$. Note different scales on the source contributions.

3.3 Setting up a multiple linear regression

As the OP is a value of reactivity, it cannot be directly introduced in a mass-balance model. Hence, in order to estimate the contributions of the PM sources to the OP, we must use an inversion method. Despite the possible non linearity of OP values with increasing masses of PM, as discussed below, we assume in this work that the OP is linearly linked to the mass. Thus, we hereafter assume that OP and the explanatory variables, namely the mass of the PM sources m_{PM}, are linearly related as follows

$$\mathrm{OP_{obs}} = m_{PM} \cdot \beta + \varepsilon \tag{1}$$

where OP$_\text{obs}$ is the $(n \times 1)$ observed OP matrix in $\text{nmol}\,\text{min}^{-1}\,\text{m}^{-3}$, m$_\text{PM}$ the $(n \times (p+1))$ matrix with the PM mass attributed
to each source expressed in $\mu\text{g}\,\text{m}^{-3}$ and a constant unity term with no unit for the intercept, and ε the $(n \times 1)$ uncertainty matrix
in $\text{nmol}\,\text{min}^{-1}\,\text{m}^{-3}$; n is the number of samples and p the number of sources. The estimator β (matrix $(p+1) \times 1$) represents
the intrinsic OP of the sources (i.e. the OP per mass unit of PM attributed to a given source) and the intercept, expressed
respectively in $\text{nmol}\,\text{min}^{-1}\,\mu\text{g}^{-1}$ for the intrinsic OP and in $\text{nmol}\,\text{min}^{-1}\,\text{m}^{-3}$ for the intercept.

The optimal approximation of a solution for the linear system expressed by equation 1 is typically found by least squares.
A variety of methods exist differing on the function to be minimized and on the regularization or sparsity penalty imposed
to perform variable selection on β, from ordinary least squares to ridge regression and LASSO (least absolute shrinkage and
selection operator). Here we have chosen a Weighted Least Squares (WLS) approach as it has an integrated way to handle
the OP uncertainties. We have also chosen not to add a penalty function as we do not have prior knowledge on the intrinsic
OP values. However, regular WLS do not rule out negative solutions, which should be implemented in our case since it is
not demonstrated that intrinsic OP negative values exist in the real world. Therefore, a stepwise regression is conducted. The
underlying algorithm is

1. Solve the WLS problem and estimate the intrinsic OP,

2. If an intrinsic OP is negative, then set it to zero and go back to step 1,

3. Repeat until all intrinsic OPs are positive or zero.

No source is discarded based on its p-value but only if its intrinsic OP is negative. We did not choose a direct non-negative
least square approach as it would be a constraint in the model we believe is too strong. In addition, we can use the absence
of negative coefficients as a test for the coherence of our dataset. Such approach may allow us to investigate which sources
present a negative OP and why. This loop converges in a finite number of iterations, either to a situation with zero sources –
which would be discarded as absurd, pointing to a breakdown of the underlying assumptions, or to an acceptable solution with
a lower number of sources. In our particular case, since OP measurements never display negative values or negative source
contributions from the PMF, the method is strictly guaranteed to converge to an acceptable solution. Further, we expressly do
not set the intercept to zero in Eq. 1, choosing instead to use this as a check on our method. If the system is well constrained
(i.e. no missing sources) the intercept should be close to zero within the model uncertainties, without any explicit constraint.
The reciprocal situation could point to missing explanatory variables.

The uncertainties of the intrinsic OP are extracted from the variance of β, which in turn is derived from the Hessian matrix of
the WLS regression in the standard way. However, the uncertainties on the modelled OP are not analytically computed. Indeed,
some coefficients present co-variation due to the activity of the sources in the very same period of the year, so analytical
variance cannot be used to estimate uncertainties. Therefore, in order to estimate the uncertainties of the modelled OP, we
bootstrap the solution β 1000 times with a Monte-Carlo algorithm. The bootstrap simply selects randomly an intrinsic OP for
each source according to their respective normal distribution.

The algorithm was implemented in Python 3 making use of the *statsmodels* WLS module (Seabold and Perktold, 2010).

The method proposed here is an improvement of the one of Bates et al. (2015) and our methods differ in several points. First of all, our backward elimination criteria is based on the negativity of a source and not in its p-value. Indeed, a source might present a statistically significant negative value. But according to us, a source with negative intrinsic OP does not have a geo-chemical sense as the air is known to be a strong oxidant milieu. Secondly, as Bates et al. (2015) didn't measure the uncertainty of their OP samples, they used an ordinary least square (OLS) regression. On the opposite, we have an estimation of our measurements uncertainty thanks to triplicate. We then use a weighted least square (WLS) regression instead. Finally, we propose a way to estimate uncertainties of our estimated OP with a Monte-Carlo method, which is not provided in the previous study. Moreover, the method proposed here does not only included the multiple linear regression (MLR) but also the use of the PMF model instead of the CMB one. Indeed, the MLR is highly sensitive to the explanatory variable and we decide to use the local sources' profile (PMF) instead of the chemical mass balance method with ensemble-averaged source impact profiles.

3.4   Application to the Chamonix site and discussion

Figure 4 shows the comparison between observed and modelled OPs for the measurements at the Chamonix site for both OP AA and OP DTT assays. Table 2 presents the intrinsic OP AA and OP DTT in $\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for each source with their respective uncertainties and p-values.

3.4.1   Accuracy of the model

The method developed in this study appears to be sufficiently accurate to explain the two OP annual series at Chamonix. First, the seasonal trend of the OP is very well reproduced, despite some under-estimation of some of the highest values in winter. Second, the intercept of the equation regression for OP $\mathrm{AA_v}$ is not significant (p>0.05). It is not so clear for the DTT test, but the p-value remains high (p=0.04). We can consider the intercepts of the equation regression as nearly negligible (see Table 2). The PM sources presented in this study are then sufficient to explain the observed OP $\mathrm{AA_v}$ and OP $\mathrm{DTT_v}$ time series. We can also note that none of the sources was excluded for the DTT assay during the inversion procedure due to negative contributions. It emphasizes the fact that the sources explain well the observed OP. However, one source was discarded for the AA assay: the crustal dust. Its p-value was less than 0.01 for an intrinsic OP of $-0.05\pm0.01\ \mathrm{nmol\,min^{-1}\,\mu g^{-1}}$. We supposed that the crustal dust source in this study is a mixing of several sources, including Saharan dust and road suspension dust. We could then end-up with a mixing of highly different redox-active compounds towards AA test that could explain the error for this source. Further work is needed to understand this behavior.

3.4.2   Uncertainties and residual

The uncertainties of the modeled OP are quite low and mostly in the range of the measurement uncertainties (Figure 4). Indeed, the distribution of the residual is close to the normal law (Figure 5). However, we can note an asymmetry toward underestimation and residual seem to increase almost linearly with the endogenous variable (no random repartition around 0

30   for the highest OP). The OP is underestimated by the model for these days featuring concentrations. It may suggest either non-linearity with high loading (as suggested above), or particular event that is not apportioned by the sources provided in this study.
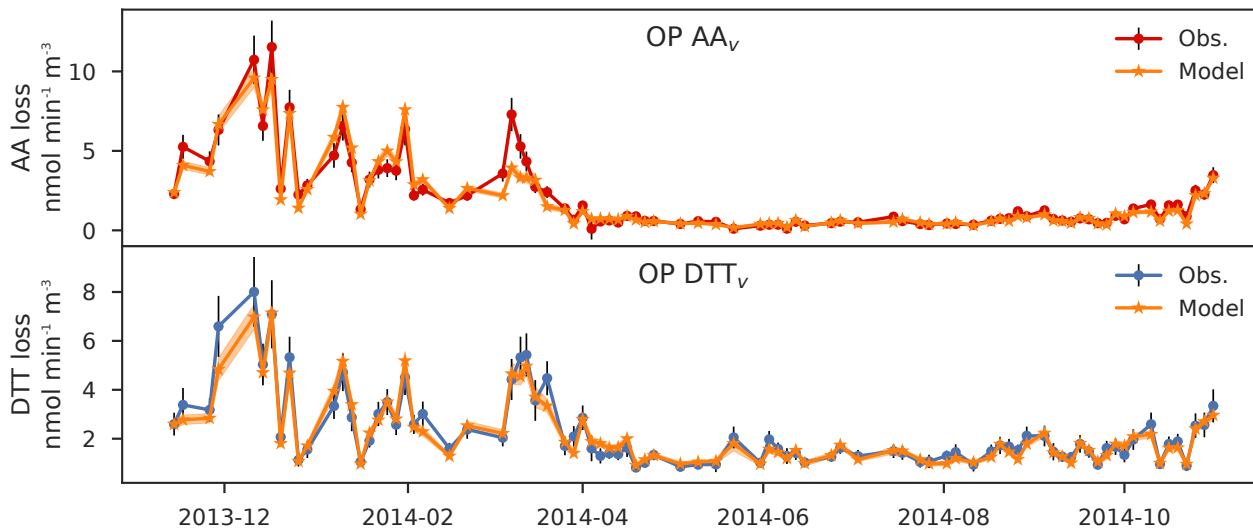

Figure 4. Comparison of the modelled OP (orange) and the observed OP for both the AA (top graph) and DTT (bottom graph) test (85 samples) from November 2013 to November 2014. The black error bars are the standard deviation of the observed values and the shaded orange area the uncertainties of the modelled OP. Units are in OP normalized by volume and expressed in $\mathrm{nmol\,min^{-1}\,m^{-3}}$.

3.4.3 Intrinsic OP

Values of the intrinsic OP of different sources for both the AA and DTT assays are ranging from zero to $0.18 \pm 0.01\ \mathrm{nmol\,min^{-1}\,\mu g^{-1}}$

5   for the AA test and from $0.06 \pm 0.02\ \mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ to $0.27 \pm 0.03\ \mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for the DTT test (Table 2). The various sources do not have the same ~~ability to generate ROS~~<u>reactivity toward the AA and DTT</u>. We also note that the two tests present different intrinsic OP for the same source, and the relative importance of the sources differs from one test to the other. For instance, the vehicular source displays a lower intrinsic OP ($0.15\ \mathrm{nmol\,min^{-1}\,\mu g^{-1}}$) than the biomass burning ($0.18\ \mathrm{nmol\,min^{-1}\,\mu g^{-1}}$) for the AA test but a higher intrinsic OP for the DTT test ($0.27\ \mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for the vehicular

10   and $0.07\ \mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ for the biomass burning). This deconvolution method may be able to account for the chemical specificity of the two OP assays. In addition, the DTT test seems to be more multi-sources influenced than the AA test.

Nevertheless, we clearly see the importance of the vehicular source, which is associated to a strong intrinsic OP in both the AA and DTT assays. Previous studies (Bates et al., 2015; Fang et al., 2016; Verma et al., 2014) also highlighted the importance of this source to explain the OP AA and DTT. We may explain such high intrinsic OP by the presence of metals in this source

15   – notably the copper (Charrier et al., 2015).
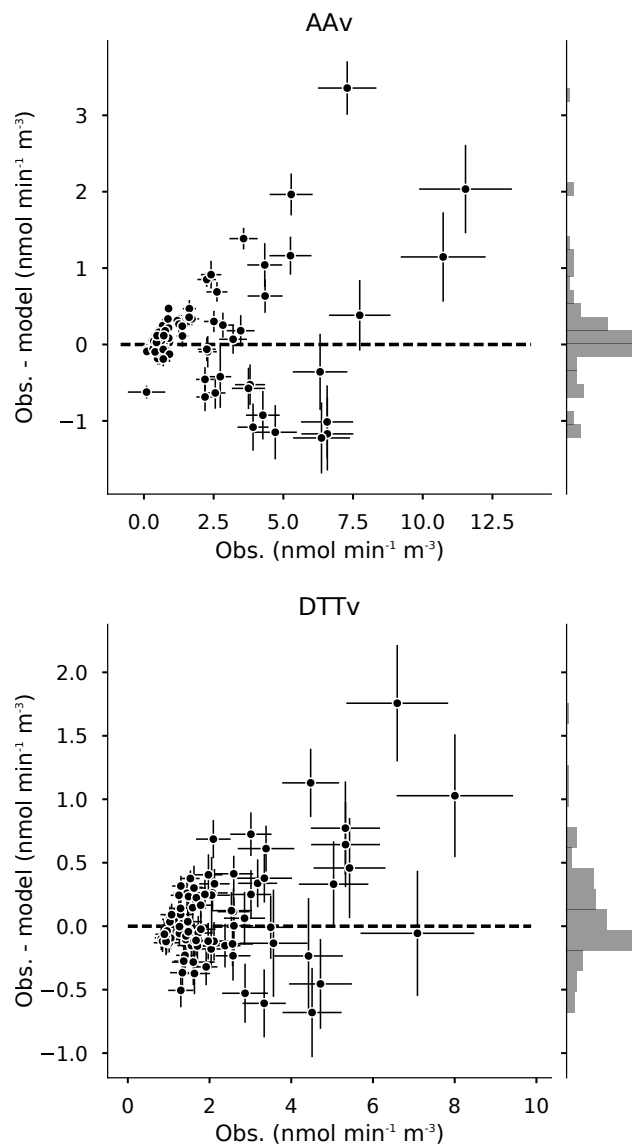
11

Figure 5. Residual distribution for the regression of the AA and DTT assays (85 samples). The error bars represent the standard deviation of the observation and the model. The histogram on the right is the distribution of the residuals. Units are in OP normalized by volume and expressed in $\mathrm{nmol\,min^{-1}\,m^{-3}}$. Note different scales for the $\mathrm{AA_v}$ and the $\mathrm{DTT_v}$.

In the AA assay, the biomass burning also presents a high redox-activity per µg of PM. This result disagrees with Fang et al. (2016) as they found no activity for this source in the OP AA test. Such difference for the biomass burning source may be explained by the two extraction protocols (in water or in a SLF solution) or by the proximity of the biomass source in Chamonix compared to the longer distance transport in Atlanta, that would change the chemistry of the source profile. However, the biomass burning in the OP DTT test has an intrinsic OP of $0.07\pm0.01\ \mathrm{nmol\,min^{-1}\,m^{-3}}$, which is coherent with

Table 2. Regression coefficients (i.e. intrinsic OP) expressed in $\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$ at Chamonix for the AA and DTT assays. The values are the mean±standard deviation based on N=1000 bootstrap of the best solution. The p-value is in the parenthesis. The crustal dust source was excluded during the inversion process for the AA test.

	Biomass burning	Crustal dust	Nitrate rich	Primary biogenic	Sea/road salt	Secondary biogenic	Sulfate rich	Vehicular	Intercept
Unit				$\mathrm{nmol\,min^{-1}\,\mu g^{-1}}$					$\mathrm{nmol\,min^{-1}\,m^{-3}}$
AA	0.18±0.01	-	0.12±0.02	0.07±0.01	0.03±0.01	0.02±0.04	0.00±0.01	0.15±0.02	0.05±0.08
	(<0.001)	(-)	(<0.001)	(<0.001)	(0.140)	(0.598)	(0.942)	(<0.001)	(0.502)
DTT	0.07±0.01	0.07±0.02	0.07±0.02	0.12±0.02	0.14±0.03	0.18±0.05	0.06±0.02	0.27±0.03	0.17±0.08
	(<0.001)	(0.003)	(<0.001)	(<0.001)	(<0.001)	(<0.001)	(<0.001)	(<0.001)	(0.045)

the previous study of Fang et al. (2016). The presence of oxygenated compounds such as quinones which are redox-active in the organic matter could explain this high intrinsic OP.

The nitrate-rich source also appears to contribute in the redox-activity in both assays. Although the nitrate itself is not redox-active, it can be present with species that are oxidants. More work is needied in order to understand the evolution of intrinsic OP for the nitrate rich factor, including measurements on series characterized by specific spring events related to agricultural activities, and series close to traffic sites for NO_x emissions.

The primary biogenic source, mainly identified by the presence of polyols, presents a significant intrinsic OP. This result was unexpected. Indeed, Liu et al. (2010) shows that mannitol is a strong anti-oxidant. Our result suggests that some chemical species, present in the primary biogenic source but not measured in this study, may contribute to the OP of the PM from this source. Recently, it was shown that fungal spores exhibit a significant intrinsic OP (Samake et al., 2017), and this may be an hypothesis to be further tested. However, the PMF profile of the primary biogenic source may also be a mixing of different sources in our study (there is BC_{ff} in it for instance). Such mixing may also explain the high intrinsic OP of this source.

Nevertheless, all these results contrast with those from simple univariate correlations between OP and sources. Indeed, the secondary biogenic source which is slightly anti-correlated to both OP's is in fact the second most redox-active source when considering intrinsic OP DTT. On the contrary, the sulfate-rich factor is slightly anti-correlated to the OP AA_v but present an intrinsic OP AA close to 0. The vehicular factor, which highly correlates with OP's is also the dominant source in terms of intrinsic OP's for both assays. Such results emphasize the real interest to go replace the simple univariate correlation by a more comprehensive statistical analysis when considering the contribution of the sources (or species) to the OP's.

3.4.4 Contribution to the OP

The aim of this study was to establish a deconvolution model for the OP. The results obtained with it will be discussed in depth in another study, including other sites. However, here are some preliminary results for the Chamonix station concerning the sources contribution.

Due to the different intrinsic OP of the sources, the source contributions to the OP (intrinsic OP times by the source contribution in $\mu g\,m^{-3}$) is different from their contribution to the PM mass. Figure 6 illustrates the normalized contribution of the sources to the mass of the aerosols and the OP measures with AA and DTT. It shows that the vehicular source barely contributes to 17 % of the total PM mass during March-April-May (MAM) and June-July-August (JJA) but more than 30 % to the OP DTT_v in the same period, and even reaching around 50 % of the OP AA_v in JJA. Conversely, some sources largely contributing to the PM_{10} mass such as the sulfate-rich source (30 % of the total PM mass in JJA) do not contribute to the OP (2 % to the OP AA_v in the same period). Finally, some sources like the biomass burning contribute to a large extend in both PM mass and OP (on an annual basis: 35 % of the PM mass, 55 % of the OP AA_v and 22 % of the OP DTT_v). We also note that on an annual basis, the contribution of the vehicular source is much larger for both OP assays than for the mass. All these outcomes are key parameters for policy initiatives.

To sum up, with this methodology, we observe a redistribution of the relative importance of the sources ranked as ROS contributors. This study gives, and more generally, the OP gives us a new vision of the atmospheric aerosols and associated ROS burden. We also point out a clear distinction between the different OP tests. Such differences raise new questions on OP assays choices and standardization and require further investigation, especially coupled OP-toxicology-epidemiology studies.
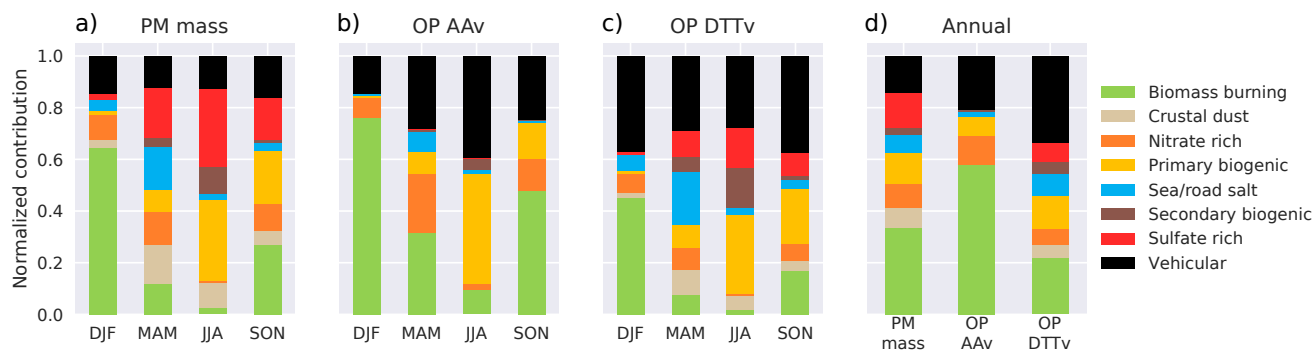

Figure 6. Normalized seasonal contribution of the sources to a) the PM_{10} total mass, b) the OP AA_v and c) the OP DTT_v. DJF is December-January-February, MAM is March-April-May, JJA is June-July-August and SON is September-October-November. d) annual normalized contributions of each source to the PM, OP AAv and OP DTTv.

4   Limitations

First of all, when comparing with others previous studies we should note that our PM extraction of samples were done in a SLF and not in water. This induces a difference in OP measurement which is not predictable for the complexes occurring between PM and SLF compounds as when PM enters in contact with the epithelial lung fluid (Calas et al., 2017) and then direct comparison may not be fully accurate.

The method used in this study gives very ~~good~~ robust results and is promising for practical application. However, since it has some limitations, we hereafter list some possible improvements. First, as previously discussed, the model is strongly

constrained by the explanatory variable, which are the PM sources contributions obtained with a PMF analysis. The PMF model has uncertainties of two different natures, inherent to the model: 1) mathematical uncertainties on the sources contributions and 2) frequent mixing profiles, due to co-linearity induced, e.g., mainly by meteorology. In our study, we might encounter such mixing for the biogenic sources. An improvement would be to bootstrap the PMF results and use these uncertainties in the OP

5   inversion in order to see its sensitivity.

Even if it has been shown that mainly $PM_{2.5}$ deposit in lung alveoli (Fang et al., 2017), PM_{10} are still a public health concern and under regulation in EU and France. PM_{10} has the advantage to encompass all parts of PM potentially reaching the lower respiratory track. However, in doing so, a source of uncertainty probably arises from the mixing, in our measurements systems, of PM populations with different chemical characteristics (i.e. acidity), that can influence the OP (i.e. changing solubility of

10   trace metal, for example).This potential artifact, already existing for $PM_{2.5}$, may be reinforced with PM_{10}.

Another debatable choice is setting the intrinsic OP to zero for the source with a negative intrinsic OP during the stepwise regression process. Some chemical species may act as anti-oxidants which lead to "negative" intrinsic OP for the associated PM source. Namely, the polyols from the primary biogenic source, that include species like mannitol, are known to present strong anti-oxidant capabilities (Liu et al., 2010) and bacteria can halve the OP of copper-rich PM (Samake et al., 2017).

15   Further studies should focus on this topic in order to better understand this potential effect.

Other choices of targets for optimization, and of penalty functions to promote the positivity of the coefficients, are possible. However, we think that our proposals manage to strike a balance between a satisfactory handling of the uncertainties of the problem and ease of application using existing statistical frameworks.

5   Conclusions

20   Based on one-year PM_{10} sampling at an urban site located in Chamonix (France) associated with chemical speciation and Oxidative Potential (OP) measurements with the DTT and OP AA assays, we successfully established a method to attribute the contribution of the PM sources to the observed OP. The main ~~conlusions~~ conclusions of this study are summarized hereafter:

1. The different sources present different OP AA and OP DTT per microgram of PM with intrinsic OP differences between sources up to a factor of 20.

25   2. The biomass burning and ~~Vvhicular~~ vehicular sources seem to be the leading sources of the OP AA_v and OP DTT_v in Chamonix. On an annual basis, they represent together 78 % of the OP AA_v and 54 % of the OP DTT_v apportionment.

3. The two OP ~~essays~~ assays present different view on the PM sources based on their specific chemical selectivity as illustrated by the salt source that does not contribute to the OP AA_v but to the OP DTT_v.

4. The relative mass contributions of the sources to the PM_{10} differ from their relative OP AA_v and OP DTT_v contributions. For instance, the vehicular source has a larger contribution to the total OP AA and OP DTT than to the total PM_{10} mass, whereas the sulfate rich source appears to be a minor source of OP AA_v but an important source of PM mass. If OP is a

proper metric of health impact of PM on population, the PM mass is not fully appropriate for PM regulations targeting public health.

5 Finally, even if OP metric is correlated to health outcomes, this study cannot directly attribute toxicity to one source or another. Is sporadic exposure to PM with high OP values or chronical exposure to PM with low OP values sufficient to provoke health damage? As the DTT and AA tests point different sources as the main ROS-generating, does one of them is the more linked to toxicological effects (if any)? To answer these questions, more cross-over studies ~~including OP-epidemiology~~ involving OP measurements, epidemiology and toxicology are needed.

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